1 Analysis of two-component non-equilibrium model of linear reactive
2 chromatography

3 Shamsul Qamar, Sameena Bibi, Noreen Akram and
4 Andreas Seidel-Morgenstern

7 **Abstract** This article presents semi-analytical solutions and analytical temporal moments of a
8 two-components linear reactive lumped kinetic model incorporating irreversible ($A \to B$) and
9 reversible ($A \leftrightarrows B$) reactions in a fixed-bed liquid chromatographic column. Both solid and liquid
10 phase reactions and two sets of boundary conditions are considered. The current model equations
11 contain a coupled system of two partial differential equations (PDEs) and two ordinary differential
12 equations (ODEs). The solution methodology successively employs the Laplace transform and
13 linear transformation steps to uncouple the governing set of coupled differential equations. The
14 resulting system of uncoupled ODEs is solved by applying an elementary solution technique.
15 The numerical Laplace inversion is employed to transform back the solutions in the actual time
16 domain. To further analyze the effects of different kinetic parameters, statistical temporal moments
17 are derived from the Laplace transformed solutions. The current solutions extend and generalize
18 our recent solutions for single-solute transport models of non-reactive liquid chromatography. For
19 verification, the analytical results are compared with the numerical solutions of a high resolution
20 finite volume scheme. Several case studies of practical interest are considered. Good agreements
21 in the results validate the correctness of semi-analytical solutions and the accuracy of proposed
22 numerical algorithm.

23 **Keywords** Liquid chromatography, non-equilibrium transport, irreversible and reversible
24 reactions, mass transfer, analytical solutions, moment analysis.

25 1 introduction

26 Column liquid chromatography is one of the most effective means of separation which is mainly
27 used for the separation of components employed as fine chemicals, pharmaceuticals, food additives
28 and biological products. The demand for efficient preparative and large-scale liquid chromato-
29 graphic separation processes is ever increasing. The concept is successfully applied to perform
30 numerous difficult separation processes, for example the separation of enantiomers and the isola-
31 tion of specific proteins from fermentation broths. In the column liquid chromatography, a mobile
32 phase percolates through a bed of fixed porous particles, carrying the mixture components which

S. Qamar, N. Akram
Department of Mathematics, COMSATS Institute of Information Technology, Park Road Chak Shahzad Islamabad,
Pakistan
Tel.: +92 51 8318471
Fax: +92 51 8318499
E-mail: shamsul.qamar@comsats.edu.pk
S. Bibi
Department of Mathematics, Air University, PAF Complex, Sector E-9 Islamabad, Pakistan

S. Qamar, A. Seidel-Morgenstern
Max Planck Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, 39106 Magdeburg, Germany

interact differently with the stationary phase. Components interacting strongly with the particles transport (elute) slowly along the column as compared to the components having weaker interactions. Therefore, each component forms a concentration band profile moving with a specific velocity in the column. These velocity differences make possible, for a long enough column, to collect pure fractions of components at the outlet of the column [1–3].

The coupling of chemical or biochemical reactions and chromatographic separations leads to an integrated process for the production of high purity products. Within a chromatographic reactor the conversion of the reactants and the separation of the components takes place simultaneously. Therefore, reversible reactions can overcome the limitation of the conversion ruled by a chemical equilibrium. The reaction within integrated processes can be catalyzed either homogeneously or heterogeneously. In the case of a homogeneous catalysis the separation of the catalyst from the products has to be taken into account. Heterogeneously catalyzed reactions occur more often. In special cases, such as esterifications, the same ion exchange resin can act as catalyst for the reaction as well as adsorbent for the separation [4]. In contrast to the sequentially connected conventional reactors and separators, chromatographic reactors effectively reduce the number of units and improve the conversion, yield and separation capacity. Chromatographic reactors were studied by several authors [1,5–23]

Mathematical modeling and numerical analysis of chromatographic operations have received considerable attention since the late 1960s. A variety of mathematical models of various degree of complexity have been introduced in chromatography. For systems where equilibrium and mass transfer processes are represented by linear relationships, analytic solutions of the models are possible in the Laplace domain [24]. The analytical back transformations of the Laplace domain solutions are only possible in simplified situations [25]. However, numerical Laplace inversion techniques can be employed to calculate peak profiles from the analytical solution in the Laplace domain [26,27]. The moment generating property of the Laplace-domain solutions can be utilized to calculate moments of chromatographic peaks. Therefore, the retention time, the peak width, the number of theoretical plates, the peak asymmetry, and other chromatographic parameters of interest can be calculated using algebraic expressions. The moment analysis has been used in a number of studies of fixed-bed systems [3,24,28–33].

In this work, the semi-analytical solutions and analytical temporal moments are derived for two-components reactive lumped kinetic model (RLKM) considering irreversible ($A \rightarrow B$) and reversible ($A \leftrightarrows B$) reactions in the liquid and solid phases. Moreover, two sets of boundary conditions are considered for a rectangular pulse injection of finite width. The current work is an extension of our previous analysis for simplified models [31,32,34]. The solution procedure successively employs the Laplace transform and eigen-decomposition technique to uncouple the governing set of coupled differential equations. The resulting uncoupled systems of ODEs are solved using an elementary solution technique. For further analysis of the process, the analytical temporal moments are derived from the Laplace transformed solutions [31,35–37]. In the current situation, the analytical Laplace inversion is not possible. Therefore, the numerical Laplace inversion is applied to get back the solution in the actual time domain [26,27]. To verify the correctness of analytical results, the high-resolution finite volume scheme (HR-FVS) is applied to solve the model equations numerically [22,38]. Several case studies are carried out and analytical results are compared with those determined numerically. Good agreements in the results verify the correctness of analytical results and accuracy of the suggested numerical algorithm.

The rest of the paper is organized as follows. In Section 2, the RLKM is introduced and analytically solved for irreversible reactions. Section 3 extends this analysis to the case of reversible reaction. Section 4 presents the derivation of analytical moments for both types of reactions and two sets of boundary conditions. In Section 5, several case studies are carried out. Finally, conclusions are drawn in Section 6.

2 Irreversible reaction (A→B)

A one-dimensional two-component transport model of linear reactive chromatography is considered. In this process, the component A (component 1) converts into B (component 2) through an first order irreversible reaction having reaction rate constants η in the liquid phase and ν in the solid phase. The semi-analytical solutions of the model are obtained for different sets of inlet and outlet boundary conditions by means of Laplace transformation. Here, the solution procedure of Quezada et al. [35] is adopted to solve the model equations. Let t represents the time coordinate and z denotes the axial coordinate along the column length. Moreover, it is assumed that the axial dispersion coefficient, denoted by D_z, is same for both components. The lumped kinetic model incorporates the rate of variation of the local concentration of solute in the stationary phase. The model lumps hereby the contribution of internal and external mass transport resistances into a mass transfer coefficient. Thus, the mass balances in the liquid phase of a two-component linear RLKM can be expressed as

$$\frac{\partial c_1}{\partial t} + u\frac{\partial c_1}{\partial z} = D_z\frac{\partial^2 c_1}{\partial z^2} - \frac{k_1}{\epsilon}(q_1^* - q_1) - \eta_1 c_1 \,, \tag{1}$$

$$\frac{\partial c_2}{\partial t} + u\frac{\partial c_2}{\partial z} = D_z\frac{\partial^2 c_2}{\partial z^2} - \frac{k_2}{\epsilon}(q_2^* - q_2) + \eta_1 c_1 \,. \tag{2}$$

For the solid phase, the governing equations are given as

$$\frac{\partial q_1}{\partial t} = \frac{k_1}{1-\epsilon}(q_1^* - q_1) - \nu_1 q_1 \,, \tag{3}$$

$$\frac{\partial q_2}{\partial t} = \frac{k_2}{1-\epsilon}(q_2^* - q_2) + \nu_1 q_1 \,. \tag{4}$$

Appropriate boundary conditions at both ends of the column are also required which will be presented while deriving analytical solutions. In above equations, c_i denotes the liquid phase concentration of i-th component, q_i represents the solid phase concentration of i-th component, and k_i is the mass transfer coefficient of i-th component. The linear adsorption isotherm for the i-th component equilibrium solid phase concentration is given as $q_i^* = a_i c_i$, a_i represents the Henry constant, and $\epsilon \in (0, 1)$ is the external porosity. Moreover, η_i and ν_i are the i-th component liquid and solid phases reaction rate constants, respectively. The RLKM takes into account the mass transfer kinetics in the solid phase that makes it more accurate than the reactive equilibrium dispersive model (REDM) which assumes equilibrium in the solid phase concentration. For large values of k_i $(i = 1, 2)$, the solution of RLKM converges to that of REDM. To simplify the notations and reduce the number of variables, the following dimensionless variables are introduced:

$$x = \frac{z}{L_{\max}}, \qquad \tau = \frac{ut}{L_{\max}}, \qquad Pe = \frac{L_{\max}u}{D_z}, \qquad \widetilde{\eta}_i = \frac{L_{\max}\eta_i}{u}, \qquad \widetilde{\nu}_i = \frac{L_{\max}\nu_i}{u},$$

$$\widetilde{k}_i = \frac{L_{\max}k_i}{u}, \qquad C_i = \frac{c_i}{c_0}, \qquad Q_i = \frac{q_i}{c_0}, \qquad c_0 = \max(c_{i,\text{inj}})\,, \quad (i = 1, 2), \tag{5}$$

where $L_{\max}$ is the length of the column. Substituting these variables into Eqs. (1) to (4), we obtain

$$\frac{\partial C_1}{\partial \tau} + \frac{\partial C_1}{\partial x} = \frac{1}{Pe}\frac{\partial^2 C_1}{\partial x^2} - \frac{\widetilde{k}_1}{\epsilon}(a_1 C_1 - Q_1) - \widetilde{\eta}_1 C_1 \,, \tag{6}$$

$$\frac{\partial C_2}{\partial \tau} + \frac{\partial C_2}{\partial x} = \frac{1}{Pe}\frac{\partial^2 C_2}{\partial x^2} - \frac{\widetilde{k}_2}{\epsilon}(a_2 C_2 - Q_2) + \widetilde{\eta}_1 C_1 \,, \tag{7}$$

$$\frac{\partial Q_1}{\partial \tau} = \frac{\widetilde{k}_1}{1-\epsilon}(a_1 C_1 - Q_1) - \widetilde{\nu}_1 Q_1 \,, \tag{8}$$

$$\frac{\partial Q_2}{\partial \tau} = \frac{\widetilde{k}_2}{1 - \epsilon}(a_2 C_2 - Q_2) + \widetilde{\nu}_1 Q_1. \tag{9}$$

109   The corresponding initial conditions in non-dimentionalize form are given as

$$C_i(0, x) = \frac{c_{\text{i,init}}}{c_0} = C_{\text{i,init}}, \quad Q_i(0, x) = \frac{a_i c_{\text{i,init}}}{c_0} = a_i C_{\text{i,init}}, \quad (i = 1, 2). \tag{10}$$

110   After applying the Laplace transform in τ domain and eliminating the Laplace transformed solid
111   phase concentration $\bar{Q}_i$ from Eqs. (6) and (7) through Eqs. (8) and (9), we obtain

$$\frac{d^2 \bar{C}_1}{dx^2} - Pe\frac{d\bar{C}_1}{dx} - (r_1 + s\alpha_1)\bar{C}_1 = (-\alpha_1 + \beta_1)C_{1,\text{init}}, \tag{11}$$

$$\frac{d^2 \bar{C}_2}{dx^2} - Pe\frac{d\bar{C}_2}{dx} + r_2 \bar{C}_1 - s\alpha_2 \bar{C}_2 = -\alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}}, \tag{12}$$

112   where

$$\alpha_1 = Pe\left[1 + \frac{a_1 F\widetilde{k}_1(s + \widetilde{\nu}_1)}{s\{(1 - \epsilon)(s + \widetilde{\nu}_1) + \widetilde{k}_1\}}\right], \quad \alpha_2 = Pe\left[1 + \frac{a_2 F\widetilde{k}_2}{s(1 - \epsilon) + \widetilde{k}_2}\right], \quad F = \frac{1 - \epsilon}{\epsilon},$$

$$r_1 = Pe\widetilde{\eta}_1, \quad r_2 = Pe\left[\widetilde{\eta}_1 + \frac{a_1 F\widetilde{\nu}_1 \widetilde{k}_1 \widetilde{k}_2}{\{(1 - \epsilon)(s + \widetilde{\nu}_1) + \widetilde{k}_1\}\{s(1 - \epsilon) + \widetilde{k}_2\}}\right],$$

$$\beta_1 = \frac{Pea_1 F\widetilde{\nu}_1 \widetilde{k}_1}{s\{(1 - \epsilon)(s + \widetilde{\nu}_1) + \widetilde{k}_1\}}, \quad \beta_2 = \frac{Pea_1 F\widetilde{\nu}_1 \widetilde{k}_2(1 - \epsilon)}{\{(1 - \epsilon)(s + \widetilde{\nu}_1) + \widetilde{k}_1\}\{s(1 - \epsilon) + \widetilde{k}_2\}}. \tag{13}$$

113   In these equations, $\bar{C}_1$ and $\bar{C}_2$ are the liquid phase concentrations of mixture components in the
114   Laplace domain. By using matrix notation, Eqs. (11) and (12) take the following form

$$\frac{d^2}{dx^2}\left\{\begin{matrix} \bar{C}_1 \\ \bar{C}_2 \end{matrix}\right\} - Pe\frac{d}{dx}\left\{\begin{matrix} \bar{C}_1 \\ \bar{C}_2 \end{matrix}\right\} + \begin{bmatrix} -r_1 - s\alpha_1 & 0 \\ r_2 & -s\alpha_2 \end{bmatrix}\left\{\begin{matrix} \bar{C}_1 \\ \bar{C}_2 \end{matrix}\right\} = \left\{\begin{matrix} (-\alpha_1 + \beta_1)C_{1,\text{init}} \\ -\alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}} \end{matrix}\right\}, \tag{14}$$

115   where parenthesis [   ] stands for a square matrix and {   } represents the column matrix. Thus,
116   a combined reaction coefficient matrix $[B]$ on the left hand side of Eq. (14) is given as
117

$$B = \begin{bmatrix} -r_1 - s\alpha_1 & 0 \\ r_2 & -s\alpha_2 \end{bmatrix}. \tag{15}$$

118   Next, we compute the linear transformation matrix $[A]$. Note that, the columns of $[A]$ should be
119   the eigenvectors of the combined reaction coefficient matrix $[B]$. The eigenvalues and eigenvectors
120   of $[B]$ are given as:
121

$$\lambda' = -r_1 - s\alpha_1, \quad x_1 = \begin{bmatrix} A_{11} \\ \frac{r_2 A_{11}}{s(\alpha_2 - \alpha_1) - r_1} \end{bmatrix} \quad \text{and} \quad \lambda'' = -s\alpha_2, \quad x_2 = \begin{bmatrix} 0 \\ A_{22} \end{bmatrix}. \tag{16}$$

122   Here, λ' and λ'' are the eigenvalues and A_{11} and A_{22} are the arbitrary constants. For simplicity,
123   we take the values of A_{11} and A_{22} equal to one. Then, using Eq. (16), the diagonal matrix $\widetilde{P}$ and
124   the transformation matrix $[A]$ can be written as
125

$$\widetilde{P} = \begin{bmatrix} -r_1 - s\alpha_1 & 0 \\ 0 & -s\alpha_2 \end{bmatrix}, \quad A = \begin{bmatrix} 1 & 0 \\ \frac{r_2}{s(\alpha_2 - \alpha_1) - r_1} & 1 \end{bmatrix}. \tag{17}$$

126   The matrix $[A]$ can be used for the following linear transformation
127

$$\left\{\begin{matrix} \bar{C}_1 \\ \bar{C}_2 \end{matrix}\right\} = \begin{bmatrix} 1 & 0 \\ \frac{r_2}{s(\alpha_2 - \alpha_1) - r_1} & 1 \end{bmatrix}\left\{\begin{matrix} b_1 \\ b_2 \end{matrix}\right\}. \tag{18}$$

128 By applying the above linear transformation on Eq. (14) we get

$$\frac{d^2}{dx^2}\left\{\begin{matrix} b_1 \\ b_2 \end{matrix}\right\} - Pe\frac{d}{dx}\left\{\begin{matrix} b_1 \\ b_2 \end{matrix}\right\} + \begin{bmatrix} -r_1 - s\alpha_1 & 0 \\ 0 & -s\alpha_2 \end{bmatrix}\left\{\begin{matrix} b_1 \\ b_2 \end{matrix}\right\}$$

$$= \begin{bmatrix} 1 & 0 \\ \frac{-r_2}{s(\alpha_2 - \alpha_1) - r_1} & 1 \end{bmatrix}\left\{\begin{matrix} (-\alpha_1 + \beta_1)C_{1,\text{init}} \\ -\alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}} \end{matrix}\right\}. \tag{19}$$

129 One can see that Eq. (19) represents the two independent, steady state, advection-dispersion equa-
130 tions with decay term of first order. Next is to find the explicit solutions of these two independent
131 ordinary differential equations

$$\frac{d^2 b_1}{dx^2} - Pe\frac{db_1}{dx} - (r_1 + s\alpha_1)b_1 = (-\alpha_1 + \beta_1)C_{1,\text{init}}, \tag{20}$$

$$\frac{d^2 b_2}{dx^2} - Pe\frac{db_2}{dx} - s\alpha_2 b_2 = \frac{r_2(\alpha_1 - \beta_1)C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}}. \tag{21}$$

132 The solutions of ODEs in Eqs. (20) and (21) are given as
133

$$b_1(s,x) = A_1 e^{\lambda_1 x} + B_1 e^{\lambda_2 x} + \frac{(\alpha_1 - \beta_1)}{r_1 + s\alpha_1}, \qquad \lambda_{1,2} = \frac{Pe \pm \sqrt{Pe^2 + 4(r_1 + s\alpha_1)}}{2}, \tag{22}$$

134 and

$$b_2(s,x) = A_2 e^{\lambda_3 x} + B_2 e^{\lambda_4 x} - \frac{1}{s\alpha_2}\left[\frac{r_2(\alpha_1 - \beta_1)C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}}\right],$$

$$\lambda_{3,4} = \frac{Pe \pm \sqrt{Pe^2 + 4s\alpha_2}}{2}. \tag{23}$$

135 Here, A_1, B_1, A_2 and B_2 are integration constants which can be determined by using suitable
136 boundary conditions (BCs) at the column inlet and outlet. In this study, we consider two sets of
137 BCs as given below. If $r_i = 0$ (for $i = 1, 2$) and $\nu = 0$, Eqs. (22) and (23) reduce to non-reactive
138 chromatographic model equations discussed in Javeed et al. [31].

139 2.1 Dirichlet BCs

140 In this case, the normalized inlet BCs are given as

$$C_i(\tau, 0) = \begin{cases} \frac{c_{i,\text{inj}}}{c_0}, & \text{if } 0 < \tau \le \tau_{\text{inj}}, \qquad i = 1, 2, \\ 0, & \tau > \tau_{\text{inj}}. \end{cases} \tag{24}$$

141 At the column outlet, the Neumann BCs for a column of hypothetically infinite length are used as

$$\frac{\partial C_i}{\partial x}(\tau, \infty) = 0, \qquad i = 1, 2. \tag{25}$$

142 Here $c_{i,\text{inj}}$ denotes the injected concentration of component i at the left end of the column (i.e. at
143 $x = 0$). By assuming $C_{i,\text{inj}} = \frac{c_{i,\text{inj}}}{c_0}$ for $i = 1, 2$, these boundary conditions in the Laplace domain
144 can be expressed as

$$\bar{C}_i(s, 0) = \frac{C_{i,\text{inj}}}{s}\left(1 - e^{-s\tau_{\text{inj}}}\right), \qquad \frac{d\bar{C}_i}{dx}(s, \infty) = 0, \qquad i = 1, 2. \tag{26}$$

145 Using the transformation given in Eq. (18), we get

$$\bar{C}_1(s,x) = b_1(s,x)\,, \tag{27}$$

which gives

$$\bar{C}_1(s,0) = b_1(s,0) = \frac{C_{1,\text{inj}}}{s}\left(1 - e^{-s\tau_{\text{inj}}}\right)\,, \qquad \frac{db_1}{\partial x}(s,\infty) = 0\,. \tag{28}$$

Similarly

$$b_2(s,x) = \bar{c}_2(s,x) - \frac{r_2 b_1(s,x)}{s(\alpha_2 - \alpha_1) - r_1}\,, \tag{29}$$

so that

$$b_2(s,0) = \frac{(1 - e^{-s\tau_{\text{inj}}})}{s}C_{2,\text{inj}} - \frac{r_2 b_1(s,0)}{s(\alpha_2 - \alpha_1) - r_1}\,, \qquad \frac{db_2}{dx}(s,\infty) = 0\,. \tag{30}$$

After applying the BCs in Eq. (28) on Eq. (22), the values of A_1 and B_1 are given as

$$A_1 = 0\,, \qquad B_1 = \frac{(1 - e^{-s\tau_{\text{inj}}})}{s}C_{1,\text{inj}} - \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1}\,. \tag{31}$$

By using the relation in Eq. (27), we get the Laplace domain solution as

$$\bar{C}_1(s,x) = \left[\frac{(1 - e^{-s\tau_{\text{inj}}})}{s}C_{1,\text{inj}} - \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1}\right]e^{\lambda_2 x} + \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1}\,. \tag{32}$$

Similarly, using Eq. (30) in Eq. (23), we get the values of A_2 and B_2 as

$$A_2 = 0\,, \quad B_2 = \frac{(1 - e^{-s\tau_{\text{inj}}})}{s}\left[C_{2,\text{inj}} - \frac{r_2\,C_{1,\text{inj}}}{s(\alpha_2 - \alpha_1) - r_1}\right]$$
$$+ \frac{1}{s\alpha_2}\left[\frac{r_2(\alpha_1 - \beta_1)C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}}\right]\,. \tag{33}$$

Thus, Eq. (23) together with the values of A_2 and B_2 becomes

$$b_2(s,x) = \left[\frac{(1 - e^{-s\tau_{\text{inj}}})}{s}\left\{C_{2,\text{inj}} - \frac{r_2\,C_{1,\text{inj}}}{s(\alpha_2 - \alpha_1) - r_1}\right\} + \frac{1}{s\alpha_2}\left\{\frac{r_2(\alpha_1 - \beta_1)C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}}\right.\right.$$
$$\left.\left. - \beta_2 C_{1,\text{init}}\right\}\right]e^{\lambda_4 x} - \frac{1}{s\alpha_2}\left[\frac{(\alpha_1 - \beta_1)r_2 C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}}\right]\,. \tag{34}$$

After using Eq. (29) in Eq. (34), we obtain

$$\bar{C}_2(s,x) = \frac{r_2}{s(\alpha_2 - \alpha_1) - r_1}\left[e^{\lambda_2 x}\left\{\frac{(1 - e^{-s\tau_{\text{inj}}})}{s}C_{1,\text{inj}} - \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1}\right\} + \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1}\right]$$
$$+ e^{\lambda_4 x}\left[\frac{(1 - e^{-s\tau_{\text{inj}}})}{s}\left\{C_{2,\text{inj}} - \frac{r_2\,C_{1,\text{inj}}}{s(\alpha_2 - \alpha_1) - r_1}\right\} + \frac{1}{s\alpha_2}\left\{\frac{(\alpha_1 - Pe\beta_1)r_2 C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}}\right.\right.$$

$$- \beta_2 C_{1,\text{init}} \Big\} \Big] - \frac{1}{s\alpha_2} \left[\frac{(\alpha_1 - \beta_1)r_2 C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}} \right]. \tag{35}$$

The solutions in τ domain $C_i(\tau, x)$ can be achieved by using the following expression for the back transformation:

$$C_j(\tau, x) = \frac{1}{2\pi \ i} \int\limits_{\gamma - i\infty}^{\gamma + i\infty} e^{-\tau s} \bar{C}_j(s, x) ds, \quad j = 1, 2, \tag{36}$$

where, γ is a real constant that exceeds the real part of all the singularities of $\bar{C}_j(s, x)$.

In this case, no analytical Laplace inversion is possible. Therefore, numerical Laplace inversion is adopted to get back solutions in the actual time domain [26, 27, 31, 32]. In this technique, the exact integrals of back transformation (c.f. Eq. (36)) are approximated by using Fourier series [27].

2.2 Danckwerts boundary conditions

In this case, the finite length column is considered. The normalized boundary conditions have the form [39]

$$C_i(\tau, 0) = \begin{cases} C_{i,\text{inj}} + \frac{1}{Pe} \frac{\partial C_i}{\partial x}(\tau, 0) \,, & \text{if } 0 < \tau \le \tau_{\text{inj}} \,, \qquad i = 1, 2 \,, \\ 0 \,, & \tau > \tau_{\text{inj}} \,, \end{cases} \tag{37}$$

and

$$\frac{\partial C_i}{\partial x}(\tau, 1) = 0, \qquad i = 1, 2. \tag{38}$$

Using the Laplace transformation, we get

$$\bar{C}_i(s, 0) = \frac{(1 - e^{-s\tau_{\text{inj}}})}{s} C_{i,\text{inj}} + \frac{1}{Pe} \frac{d\bar{C}_i}{dx}(s, 0) \,, \qquad \frac{d\bar{C}_i}{dx}(s, 1) = 0 \,. \tag{39}$$

Following the same solution procedure as discussed in Subsection 2.1, the solutions in the Laplace domain are given as

$$\bar{C}_1(s, x) = \left[\frac{\lambda_2 e^{\lambda_2 + \lambda_1 x} - \lambda_1 e^{\lambda_1 + \lambda_2 x}}{(1 - \frac{\lambda_1}{Pe})\lambda_2 e^{\lambda_2} - (1 - \frac{\lambda_2}{Pe})\lambda_1 e^{\lambda_1}} \right] \left[\frac{(1 - e^{-s\tau_{\text{inj}}})}{s} C_{1,\text{inj}} - \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1} \right]$$
$$+ \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1} \,, \tag{40}$$

and

$$\bar{C}_2(s, x) = \left[\frac{r_2}{s(\alpha_2 - \alpha_1) - r_1} \right] \left[\frac{\lambda_2 e^{\lambda_2 + \lambda_1 x} - \lambda_1 e^{\lambda_1 + \lambda_2 x}}{(1 - \frac{\lambda_1}{Pe})\lambda_2 e^{\lambda_2} - (1 - \frac{\lambda_2}{Pe})\lambda_1 e^{\lambda_1}} \right] \left[\frac{(1 - e^{-s\tau_{\text{inj}}})}{s} C_{1,\text{inj}} \right.$$
$$\left. - \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1} \right] + \frac{(\alpha_1 - \beta_1)C_{1,\text{init}}}{r_1 + s\alpha_1} \left[\frac{r_2}{s(\alpha_2 - \alpha_1) - r_1} \right]$$
$$+ \left[\frac{\lambda_4 e^{\lambda_4 + \lambda_3 x} - \lambda_3 e^{\lambda_3 + \lambda_4 x}}{(1 - \frac{\lambda_3}{Pe})\lambda_4 e^{\lambda_4} - (1 - \frac{\lambda_4}{Pe})\lambda_3 e^{\lambda_3}} \right] \left(\frac{1 - e^{-s\tau_{\text{inj}}}}{s} \right) \left\{ C_{2,\text{inj}} - \frac{r_2 C_{1,\text{inj}}}{s(\alpha_2 - \alpha_1) - r_1} \right\}$$

$$+ \frac{1}{s\alpha_2} \left\{ \frac{(\alpha_1 - \beta_1)r_2 C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}} \right\} \right]$$

$$- \frac{1}{s\alpha_2} \left[\frac{(\alpha_1 - \beta_1)r_2 C_{1,\text{init}}}{s(\alpha_2 - \alpha_1) - r_1} - \alpha_2 C_{2,\text{init}} - \beta_2 C_{1,\text{init}} \right]. \tag{41}$$

Once again, no analytical Laplace inversion is possible. Therefore, the numerical Laplace inversion is applied to get back solutions in the actual time domain [26, 27, 31, 32].

3 Reversible reaction $A \rightleftharpoons B$

In this section, the more general case of linear reaction, i.e. reversible reaction, is presented. For the considered case, the injected component A (component 1) converts to the component B (component 2) with reaction rate constants η_1 in the liquid phase and ν_1 in the solid phase. Because of the reversible reaction, component B is converted partly back to component A with a reaction rate constant η_2 in liquid phase and ν_2 in the solid phase. Thus, the governing equations of two-components RLKM in the liquid phase are formulated as

$$\frac{\partial c_1}{\partial t} + u \frac{\partial c_1}{\partial z} = D \frac{\partial^2 c_1}{\partial z^2} - \frac{k_1}{\epsilon}(q_1^* - q_1) - \eta_1 c_1 + \eta_2 c_2 \,, \tag{42}$$

$$\frac{\partial c_2}{\partial t} + u \frac{\partial c_2}{\partial z} = D \frac{\partial^2 c_2}{\partial z^2} - \frac{k_2}{\epsilon}(q_2^* - q_2) + \eta_1 c_1 - \eta_2 c_2 \,. \tag{43}$$

For the solid phase, the governing equations are

$$\frac{\partial q_1}{\partial t} = \frac{k_1}{1 - \epsilon}(q_1^* - q_1) - \nu_1 q_1 + \nu_2 q_2, \tag{44}$$

$$\frac{\partial q_2}{\partial t} = \frac{k_2}{1 - \epsilon}(q_2^* - q_2) + \nu_1 q_1 - \nu_2 q_2 \,. \tag{45}$$

Using dimensionless variables given in Eq. (5) and linear adsorption isotherms, the above equations in normalized form can be rewritten as

$$\frac{\partial C_1}{\partial \tau} + \frac{\partial C_1}{\partial x} = \frac{1}{Pe} \frac{\partial^2 C_1}{\partial x^2} - \frac{\widetilde{k_1}}{\epsilon}(a_1 C_1 - Q_1) - \widetilde{\eta}_1 C_1 + \widetilde{\eta}_2 C_2 \,, \tag{46}$$

$$\frac{\partial C_2}{\partial \tau} + \frac{\partial C_2}{\partial x} = \frac{1}{Pe} \frac{\partial^2 C_2}{\partial x^2} - \frac{\widetilde{k_2}}{\epsilon}(a_2 C_2 - Q_2) + \widetilde{\eta}_1 C_1 - \widetilde{\eta}_2 C_2 \,, \tag{47}$$

$$\frac{\partial Q_1}{\partial \tau} = \frac{\widetilde{k_1}}{1 - \epsilon}(a_1 C_1 - Q_1) - \widetilde{\nu}_1 Q_1 + \widetilde{\nu}_2 Q_2, \tag{48}$$

$$\frac{\partial Q_2}{\partial \tau} = \frac{\widetilde{k_2}}{1 - \epsilon}(a_2 C_2 - Q_2) + \widetilde{\nu}_1 Q_1 - \widetilde{\nu}_2 Q_2. \tag{49}$$

By applying the Laplace transformation in τ domain and eliminating Eqs. (48) and (49), Eqs. (46) and (47) take the forms

$$\frac{d^2 \bar{C}_1}{dx^2} - Pe \frac{d\bar{C}_1}{dx} - (r_1 + s\alpha_1)\bar{C}_1 + r_2 \bar{C}_2 = -\beta_1 C_{1,\text{init}} - \beta_2 C_{2,\text{init}} \,, \tag{50}$$

$$\frac{d^2 \bar{C}_2}{dx^2} - Pe \frac{d\bar{C}_2}{dx} + r_3 \bar{C}_1 - (r_4 + s\alpha_2)\bar{C}_2 = -\beta_3 C_{1,\text{init}} - \beta_4 C_{2,\text{init}} \,, \tag{51}$$

where

$$\alpha_1 = Pe\left[1 + \frac{a_1 F\widetilde{k}_1}{(1-\epsilon)(s+\widetilde{\nu}_1)+\widetilde{k}_1} + \frac{a_1 F\widetilde{\nu}_1\widetilde{k}_1}{s\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}}\right.$$

$$\left. - \frac{a_1 F\widetilde{\nu}_1\widetilde{\nu}_2\widetilde{k}_1^2(1-\epsilon)}{s\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\left[\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2\right]}\right],$$

$$\alpha_2 = Pe\left[1 + \frac{a_2\widetilde{k}_2}{s\epsilon} - \frac{a_2\widetilde{k}_2^2\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}}{s\epsilon\left[\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2\right]}\right],$$

$$F = \frac{1-\epsilon}{\epsilon}, \qquad r_1 = Pe\widetilde{\eta}_1, \qquad r_4 = Pe\widetilde{\eta}_2,$$

$$r_2 = Pe\left[\widetilde{\eta}_2 + \frac{a_2 F\widetilde{\nu}_2\widetilde{k}_1\widetilde{k}_2}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2}\right],$$

$$r_3 = Pe\left[\widetilde{\eta}_1 + \frac{a_1 F\widetilde{\nu}_1\widetilde{k}_1\widetilde{k}_2}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2}\right],$$

$$\beta_1 = Pe\left[1 + \frac{a_1 F\widetilde{k}_1}{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1}\right.$$

$$\left. + \frac{a_1 F\widetilde{\nu}_1\widetilde{\nu}_2\widetilde{k}_1(1-\epsilon)^2}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\left[\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2\right]}\right],$$

$$\beta_2 = \frac{Pea_2 F\widetilde{\nu}_2\widetilde{k}_1(1-\epsilon)}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2},$$

$$\beta_3 = \frac{Pea_1 F\widetilde{\nu}_1\widetilde{k}_2(1-\epsilon)}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2},$$

$$\beta_4 = Pe\left[1 + \frac{a_2 F\widetilde{k}_2\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}}{\{(s+\widetilde{\nu}_1)(1-\epsilon)+\widetilde{k}_1\}\{(s+\widetilde{\nu}_2)(1-\epsilon)+\widetilde{k}_2\}-\widetilde{\nu}_1\widetilde{\nu}_2(1-\epsilon)^2}\right]. \tag{52}$$

The two sets of BCs introduced in Section 2 are considered again. Adopting the same solution procedure as discussed in the previous Section, we obtain the following solutions.

3.1 Dirichlet boundary conditions

In this case, the boundary conditions in Eqs. (24) and (25) are taken into account. Thus, the Laplace domain solutions are given as

$$\bar{C}_1(s,x) = e^{m_2 x}\left[\frac{\lambda_3\left(1-e^{-s\tau_{\text{inj}}}\right)(r_3 C_{1,\text{inj}}-\lambda_4 C_{2,\text{inj}})}{sr_3(\lambda_3-\lambda_4)}\right.$$

$$\left. + \frac{\lambda_3\{(\beta_1 r_3-\beta_3\lambda_4)C_{1,\text{init}}+(\beta_2 r_3-\beta_4\lambda_4)C_{2,\text{init}}\}}{\lambda_1 r_3(\lambda_3-\lambda_4)}\right]$$

$$- e^{m_4 x}\left[\frac{\lambda_4\left(1-e^{-s\tau_{\text{inj}}}\right)(r_3 C_{1,\text{inj}}-\lambda_3 C_{2,\text{inj}})}{sr_3(\lambda_3-\lambda_4)}\right.$$

$$\left. - \frac{\lambda_4\{(-\beta_1 r_3+\beta_3\lambda_3)C_{1,\text{init}}+(-\beta_2 r_3+\beta_4\lambda_3)C_{2,\text{init}}\}}{\lambda_2 r_3(\lambda_3-\lambda_4)}\right]$$

$$- \frac{C_{1,\text{init}}\{\beta_1 r_3(\lambda_2\lambda_3-\lambda_1\lambda_4)-\beta_3\lambda_3\lambda_4(\lambda_2-\lambda_1)\}}{\lambda_1\lambda_2 r_3(\lambda_3-\lambda_4)}$$

$$+ \frac{C_{2,\text{init}}\{\beta_4\lambda_3\lambda_4\,(\lambda_2 - \lambda_1) - \beta_2 r_3(\lambda_2\lambda_3 - \lambda_1\lambda_4)\}}{\lambda_1\lambda_2 r_3(\lambda_3 - \lambda_4)}, \tag{53}$$

$$\bar{C}_2(s,x) = e^{m_2 x}\left[\frac{(1 - e^{-s\tau_{\text{inj}}})\,(r_3 C_{1,\text{inj}} - \lambda_4 C_{2,\text{inj}})}{s(\lambda_3 - \lambda_4)}\right.$$
$$\left.+ \frac{\{(\beta_1 r_3 - \beta_3\lambda_4)C_{1,\text{init}} + (\beta_2 r_3 - \beta_4\lambda_4)C_{2,\text{init}}\}}{\lambda_1(\lambda_3 - \lambda_4)}\right]$$
$$- e^{m_4 x}\left[\frac{(1 - e^{-s\tau_{\text{inj}}})\,(r_3 C_{1,\text{inj}} - \lambda_3 C_{2,\text{inj}})}{s(\lambda_3 - \lambda_4)}\right.$$
$$\left.- \frac{\{(-\beta_1 r_3 + \beta_3\lambda_3)c_{1,\text{init}} + (-\beta_2 r_3 + \beta_4\lambda_3)C_{2,\text{init}}\}}{\lambda_2(\lambda_3 - \lambda_4)}\right]$$
$$- \frac{C_{1,\text{init}}\{\beta_1 r_3\,(\lambda_2 - \lambda_1) + \beta_3(\lambda_1\lambda_3 - \lambda_2\lambda_4)\}}{\lambda_1\lambda_2(\lambda_3 - \lambda_4)}$$
$$+ \frac{C_{2,\text{init}}\{\beta_4\,(\lambda_2\lambda_4 - \lambda_1\lambda_3) - \beta_2 r_3(\lambda_2 - \lambda_1)\}}{\lambda_1\lambda_2(\lambda_3 - \lambda_4)}, \tag{54}$$

where for $W = r_1 - r_4$, $R = r_1 + r_4$, $Q = \alpha_2 - \alpha_1$, $G = \alpha_1 + \alpha_2$, $P = 4(r_2 r_3 - r_1 r_4)$ and

$$\lambda_{1,2} = -\frac{1}{2}\left[R + sG \mp \sqrt{P + R^2 + s^2 Q^2 - 2sWQ}\right], \tag{55}$$

$$\lambda_{3,4} = -\frac{1}{2}\left[W - sQ \mp \sqrt{P + R^2 + s^2 Q^2 - 2sWQ}\right]. \tag{56}$$

Moreover,

$$m_{1,2} = \frac{Pe \pm \sqrt{Pe^2 - 4\lambda_1}}{2}, \quad m_{3,4} = \frac{Pe \pm \sqrt{Pe^2 - 4\lambda_2}}{2}. \tag{57}$$

Analytical Laplace inversions of the above equations are very difficult. Therefore, numerical Laplace inversion is used to get the solutions in the actual domain [26, 27, 31, 32].

3.2 Danckwerts boundary conditions

Now, the BCs given in Eqs. (37) and (38) are taken into account. The Laplace domain solutions are formulated as

$$\bar{C}_1(s,x) = \frac{(1 - e^{-s\tau_{\text{inj}}})\,\lambda_3(r_3 C_{1,\text{inj}} - \lambda_4 C_{2,\text{inj}})(m_1 e^{m_1 + m_2 x} - m_2 e^{m_2 + m_1 x})}{r_3 s(\lambda_3 - \lambda_4)\{(1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2}\}}$$
$$- \frac{(1 - e^{-s\tau_{\text{inj}}})\,\lambda_4(r_3 C_{1,\text{inj}} - \lambda_3 C_{2,\text{inj}})(m_3 e^{m_3 + m_4 x} - m_4 e^{m_4 + m_3 x})}{r_3 s(\lambda_3 - \lambda_4)\{(1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4}\}}$$
$$+ \frac{\lambda_3\{(\beta_1 r_3 - \beta_3\lambda_4)C_{1,\text{init}} - (\beta_4\lambda_4 - \beta_2 r_3)C_{2,\text{init}}\}(m_1 e^{m_1 + m_2 x} - m_2 e^{m_2 + m_1 x})}{r_3\lambda_1(\lambda_3 - \lambda_4)\{(1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2}\}}$$
$$- \frac{\lambda_4\{(\beta_1 r_3 - \beta_3\lambda_3)C_{1,\text{init}} - (\beta_4\lambda_3 - \beta_2 r_3)C_{2,\text{init}}\}(m_3 e^{m_3 + m_4 x} - m_4 e^{m_4 + m_3 x})}{r_3\lambda_2(\lambda_3 - \lambda_4)\{(1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4}\}}$$
$$- \frac{C_{1,\text{init}}\{\beta_1 r_3\,(\lambda_2\lambda_3 - \lambda_1\lambda_4) - \beta_3\lambda_3\lambda_4(\lambda_2 - \lambda_1)\}}{\lambda_1\lambda_2 r_3(\lambda_3 - \lambda_4)}$$
$$+ \frac{C_{2,\text{init}}\{\beta_4\lambda_3\lambda_4\,(\lambda_2 - \lambda_1) - \beta_2 r_3(\lambda_2\lambda_3 - \lambda_1\lambda_4)\}}{\lambda_1\lambda_2 r_3(\lambda_3 - \lambda_4)}, \tag{58}$$

and

$$\bar{C}_2(s,x) = \frac{(1 - e^{-s\tau_{\text{inj}}})(r_3 C_{1,\text{inj}} - \lambda_4 C_{2,\text{inj}})(m_1 e^{m_1 + m_2 x} - m_2 e^{m_2 + m_1 x})}{s(\lambda_3 - \lambda_4)\{(1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2}\}}$$

$$- \frac{(1 - e^{-s\tau_{\text{inj}}})(r_3 C_{1,\text{inj}} - \lambda_3 C_{2,\text{inj}})(m_3 e^{m_3 + m_4 x} - m_4 e^{m_4 + m_3 x})}{s(\lambda_3 - \lambda_4)\{(1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4}\}}$$

$$+ \frac{\{(\beta_1 r_3 - \beta_3 \lambda_4)c_{1,\text{init}} - (\beta_4 \lambda_4 - \beta_2 r_3)C_{2,\text{init}}\}(m_1 e^{m_1 + m_2 x} - m_2 e^{m_2 + m_1 x})}{\lambda_1(\lambda_3 - \lambda_4)\{(1 - \frac{m_2}{Pe})m_1 e^{m_1} - (1 - \frac{m_1}{Pe})m_2 e^{m_2}\}}$$

$$- \frac{\{(\beta_1 r_3 - \beta_3 \lambda_3)c_{1,\text{init}} - (\beta_4 \lambda_3 - \beta_2 r_3)C_{2,\text{init}}\}(m_3 e^{m_3 + m_4 x} - m_4 e^{m_4 + m_3 x})}{\lambda_2(\lambda_3 - \lambda_4)\{(1 - \frac{m_4}{Pe})m_3 e^{m_3} - (1 - \frac{m_3}{Pe})m_4 e^{m_4}\}}$$

$$- \frac{C_{1,\text{init}}\{\beta_1 r_3 (\lambda_2 - \lambda_1) + \beta_3(\lambda_1 \lambda_3 - \lambda_2 \lambda_4)\}}{\lambda_1 \lambda_2(\lambda_3 - \lambda_4)}$$

$$+ \frac{C_{2,\text{init}}\{\beta_4 (\lambda_2 \lambda_4 - \lambda_1 \lambda_3) - \beta_2 r_3(\lambda_2 - \lambda_1)\}}{\lambda_1 \lambda_2(\lambda_3 - \lambda_4)} \,. \tag{59}$$

Here, λ_i and m_i for $i = 1, 2, 3, 4$ are given by Eqs. (55), (56) and (57). Again, the numerical Laplace inversion is applied to get the actual time domain solutions [26, 27, 31, 32].

The above models and their derived analytical solutions are considered as very flexible and versatile, both in terms of incorporated mass transfer mechanisms and regarding the option that reactions can take place independently in both phases. Many possible reactions can be treated in a simplified manner using these models. They are particularly applicable to isomerization reactions. Additionally, the important class of enantiomerization reactions, which are desired (or needed) to be suppressed in chromatographic columns, can be analyzed [41, 42].

4 Moments analysis

Moment analysis is an attractive technique for deducing important information about the retention equilibrium and mass transfer kinetics in the column. Such a moment analysis approach has been found instructive in the literature [3, 24, 31, 33]. A set of statistical temporal moments can define the appearance of the plotted elution profile. For example, the appropriate forms of the first, second and third moments can describe the mean, spread and skew of the distribution, respectively,.

The Laplace domain solutions can be utilized to obtain moments. The retention equilibrium-constant and parameters of the mass transfer kinetics in the column are related to the moments. A comparison of theoretical and experiential moments can help to estimate dispersion and other mass transfer coefficients.

In order to calculate analytical moments, the following moment generating properties of the Laplace domain solutions are exploited [31]:

The zeroth moments are defined as

$$\mu_0^{(i)} = \lim_{s \to 0}(\bar{C}_i(s, x = 1)), \quad i = 1, 2, \tag{60}$$

and the n-th moments are given as

$$\mu_n^{(i)} = (-1)^n \frac{1}{\mu_0^{(i)}} \lim_{s \to 0} \frac{d^n(\bar{C}_i(s, x = 1))}{ds^n}, \quad n = 1, 2, 3, \cdots. \tag{61}$$

In this work, the central moments up to third order are derived for both sets of BCs. A complete derivation of these moments is presented in the appendix A considering a regenerated system, i.e. $c_{i,\text{init}} = 0$ (for $i = 1, 2$), and only a solid phase reaction, i.e. $\eta_i = 0$.

222 In parallel, we integrate the concentration profiles in τ domain to compute the numerical moments.
223 The normalized n-th temporal moments of the band profiles at the outlet of chromatographic
224 column of length $x = 1$ are defined as

$$\mu_n^{(i)} = \frac{\int_0^\infty C_i(\tau, x = 1)\,\tau^n d\tau}{\int_0^\infty C_i(\tau, x = 1)d\tau}, \quad n = 0, 1, 2, \cdots, \quad i = 1, 2\,. \tag{62}$$

225 While, the n-th central moments are expressed as

$$\mu'^{(i)}_n = \frac{\int_0^\infty C_i(\tau, x = 1)\,(\tau - \mu_1^{(i)})^n d\tau}{\int_0^\infty C(\tau, x = 1)d\tau}, \quad n = 0, 1, 2, \cdots, \quad i = 1, 2\,. \tag{63}$$

226 Below in the discussion of the test problems, a comparison of analytically and numerically deter-
227 mined temporal moments will be presented. The numerical moments were obtained by integrating
228 concentration profiles generated by the high resolution FVS (c.f. Eqs. (62) and (63)) [38]. The
229 analytical expressions of $\mu'^{(i)}_2$ and $\mu'^{(i)}_3$ were very lengthy in some cases, therefore, only plots of
230 these central moments are presented. The trapezoidal rule is applied to numerically approximate
231 the integral terms appearing in these equations.

232 5 Numerical test problems

233 In this section, several test problems are presented to verify the correctness and usage of derived
234 analytical results for practical problems. For that purpose, the derived semi-analytical solutions
235 of two-components RLKM are compared with the numerical solutions of a HR-FVS [38,40]. The
236 basic parameters used in the selected test problems are listed in Table 1.

237 5.1 Irreversible reaction

238 Figure 1 shows the outlet concentration profiles after injecting a pulse of finite width in an empty
239 column ($c_{i,\text{init}} = 0\,gL^{-1}$ for $i = 1, 2$) considering Dirichlet BCs (c.f. Eqs. (24) and (25)) and
240 irreversible reaction. Here, the semi-analytical solution and the numerical solutions of HR-FVS
241 are compared. Both liquid and solid phases reactions are considered. In Figure 1a, only component
242 1 is injected (i.e. $c_{1,\text{inj}} = 1.0\,gL^{-1}$, $c_{2,\text{inj}} = 0.0\,gL^{-1}$) and the liquid phase reaction is assumed to be
243 zero, while in Figure 1b both components are injected (i.e. $c_{1,\text{inj}} = 1.0\,gL^{-1}$ and $c_{2,\text{inj}} = 0.5\,gL^{-1}$)
244 and neglecting aging the liquid phase reaction. Both plots show that reactant (component 1),
245 which has larger adsorption equilibrium constant, elutes later from the column as compared to the
246 product (component 2). On the other hand, plots in Figures 1c & 1d show the outlet concentration
247 profiles when reactions in both solid and liquid phases are considered. It can be observed from the
248 plots that the amount of component 2 further increases when the effects of both solid and liquid
249 phases reactions are considered. A good agreement between the semi-analytical and numerical
250 solutions verify the correctness of semi-analytical solutions and accuracy of the numerical solution
251 technique.
252 Figure 2 depicts the effects of rate constants on the elution profiles at the column outlet considering
253 Dirichlet BCs, $c_{i,\text{init}} = 0.0\,gL^{-1}$ (for $i = 1, 2$), $c_{1,\text{inj}} = 1.0\,gL^{-1}$, and $c_{2,\text{inj}} = 0.0\,gL^{-1}$. Figure 2a
254 displays the elution profiles for different values of the solid phase reaction rate constant, while
255 keeping the liquid phase reaction rate fixed ($\widetilde{\eta} = 0.42$ or $\eta = 0.05\,min^{-1}$). On the other hand,
256 Figure 2b shows the elution profiles for different values of liquid phase reaction rate constant,
257 while keeping the solid phase reaction rate constant fixed ($\widetilde{\nu} = 0.25$ or $\nu = 0.03\,min^{-1}$). Both
258 plots reveal that the amount of product, i.e. component 2, is increased by increasing the values
259 of reaction rate constants. Figure 3a compares the solutions for Dirichlet and Danckwerts BCs
260 considering both solid and liquid phases reactions and two different Peclet numbers (Pe). Here,

we have chosen $c_{1,\text{inj}} = 1.0\,gL^{-1}$, $c_{2,\text{inj}} = 0.0\,gL^{-1}$, $c_{i,\text{init}} = 0.0\,gL^{-1}$ (for $i = 1, 2$), and other parameters are given in Table 1. It can be observed that for smaller Pe numbers, i.e. larger axial dispersion coefficients, the effect of BCs are effective. Thus, Danckwerts BCs, which account for the back mixing, should be used in the case of large dispersion coefficient (i.e. small Pe). Figure 3b shows that the solution profiles become sharper for large values of the mass transfer coefficients k_i (for $i = 1, 2$) and become identical to solution profiles in [34]. On the other hand, the solution profiles are spreading for small values of k_i.

A quantitative comparison of moments obtained analytically, through numerical Laplace inversion, and through HR-FVS is presented in Figure 4 for a wide range of flow rates considering Dirichlet BCs, $\eta_1 = 0\,min^{-1}$, $\nu_1 = 0.03\,min^{-1}$, $c_{i,\text{init}} = 0\,gL^{-1}$ (for $i = 1, 2$), $c_{1,\text{inj}} = 1\,g/l$, and $c_{2,\text{inj}} = 0\,gL^{-1}$. To write the moments in Appendix A with dimensions, we multiplied the zeroth moments $\mu_0^{(i)}$ with $L_{\max}/u$ and the n-th moments $\mu_n^{(i)}$ with $(L_{\max}/u)^n$ (for $n = 1, 2, \cdots$). The zeroth, first, second, and third moments are plotted versus u, $1/u$, $1/u^3$, and $1/u^5$ of the derived solutions. The zeroth moment $\mu_0^{(i)}$ (for $i = 1, 2$), represent total mass of the solutes. The zeroth moments are shown in Figure 4a. The first moment, $\mu_1^{(i)}$ for $i = 1, 2$, reveal the expected linear trend of the mean retention time over $1/u$, see Figure 4b. Figure 4c displays the second central moment that quantify the variance of the solution profiles. The third central moment, $\mu'^{(i)}_3$ (for $i = 1, 2$), describing the skewness of elution profiles, is shown in Figure 4d.

Good agreements in the results demonstrate the correctness of analytical calculations and the accuracy HR-FVS. The plots for Dankwerts BCs have similar behavior and are therefore omitted. One can see that due to mass transfer coefficient considered in the RLKM, the plots of second and third central moments are little bit different from those presented in Qamar et al. [34]. However, the general trend of the moments plots is similar for Dirichlet BCs. For large values of the mass transfer coefficients k_i, the moments in Figure 4 coincide with those presented in [34] for REDM.

5.2 Reversible reaction

This part focuses on the comparison of analytical and numerical results for reversible reactions. In the presented results, only Dirichlet BCs are considered and all parameters used in the test problems are given in Table 1.

In Figure 5, the elution profile of numerical Laplace Inversion and HR-FVS are plotted after injecting a pulse of finite width in an empty column ($c_{i,\text{init}} = 0.0\,gL^{-1}$ for $i = 1, 2$). In Figure 5a, only component 1 is injected (i.e. $c_{1,\text{inj}} = 1.0\,gL^{-1}$ and $c_{2,\text{inj}} = 0.0\,gL^{-1}$), and liquid phase reaction is assumed to be zero, while in Figure 5b the injection of both components is considered (i.e. $c_{1,\text{inj}} = 1.0\,gL^{-1}$ and $c_{2,\text{inj}} = 0.5\,gL^{-1}$) and the liquid phase reaction is again neglected. On the other hand, the plots in Figures 5c & 5d show the solution profiles when reactions in both solid and liquid phases are taken into account ($\eta_1 = 0.05\,min^{-1}$, $\eta_2 = 0.1\,min^{-1}$, $\nu_1 = 0.03\,min^{-1}$ and $\nu_2 = 0.06\,min^{-1}$). Good agreements in the solution profiles validate the correctness of numerical Laplace inversion and accuracy of the HR-FVS. From these results, it is again clear that the component having larger value of adsorption equilibrium constant elutes later from the column as compared to the component having smaller value of adsorption coefficient. Because of reversible reaction, the concentration levels of both components are different as compared to the irreversible reaction case shown in Figure 1. Now, larger amount of component 1 is unconverted and lesser amount of component 2 is produced. For larger values of the mass transfer coefficients k_i ($i = 1, 2$), the solution profiles of Figure 5 become identical to those presented in [34].

Finally, a quantitative comparison of moments determined analytically, through numerical Laplace inversion and through HR-FVS is presented in Figure 6 for a wide range of flow rates considering Dirichlet BCs. Here, $c_{1,\text{inj}} = 1.0\,gL^{-1}$, $c_{2,\text{inj}} = 0.0\,gL^{-1}$, $c_{i,\text{init}} = 0.0\,g/l$ ($i = 1, 2$), $\eta_i = 0\,min^{-1}$ ($i = 1, 2$), $\nu_1 = 0.03\,min^{-1}$, and $\nu_2 = 0.06\,min^{-1}$. For the current reversible reaction, the magnitude of zeroth moment reflects the reduced conversion as compared to the results shown in Figure 4 describing the case of irreversible reaction. The trends in third central moments of components 1 and 2 depict that the component 1 is left skewed (left tailed) while the component 2 is right

311 skewed (right tailed) which can also be seen in Figure 5. Another time, a good agreement in the
312 results verify both the correctness of the analytical solutions and the high precision of proposed
313 HR-FVS. The plots for Dankwerts BCs have similar behavior and are therefore omitted.

6 Conclusion

315 The two-components linear non-equilibrium model of liquid chromatography was analyzed consid-
316 ering first order irreversible and reversible reactions in the solid and liquid phases. The considered
317 model was investigated for rectangular pulse injections of the reactants into an initially empty
318 or pre-equilibrated column using two different sets of boundary conditions. The Laplace transfor-
319 mation and eigen-decomposition technique were jointly applied solve the model equations. The
320 numerical Laplace inversions was used to get the desired concentration profiles in the actual time
321 domain. Analytical temporal moments were derived from the Laplace domain solutions. These
322 moments are helpful to investigate the amount of conversion, retention times, band broadenings,
323 and asymmetries of the elution profiles. The analytical results were compared with the numeri-
324 cal results of a HR-FVS. Good agreements between the analytically and numerically determined
325 results verified the correctness of analytical solution and the accuracy of suggested numerical al-
326 gorithm. The derived analytical solutions and moments could be useful for further developments
327 of chromatographic reactors. For instance, the analysis could be used to study the effects of mass
328 transfer and reaction kinetics on the elution profiles, for sensitivity analysis, and for validation of
329 the results obtained from newly introduced numerical schemes.

Appendix

A Analytical moments

332 Here, the analytical temporal moments are presented for two different sets of boundary conditions. For the derivation
333 of the moments, $c_{i,\text{init}} = 0\,g/l$ (for $i = 1, 2$), $\eta_i = 0$, and $c_{2,\text{inj}} = 0\,g/l$ are considered, i.e. we are considering an
334 empty column initially and injecting only component 1 into the reactor. Moreover, only the effect of solid phase
335 reaction is taken into account, while the liquid phase reaction is neglected.

A.1 Irreversible reaction and Dirichlet BCs

337 Here, we neglect the liquid phase reaction, i.e. $\eta_1 = 0\,min^{-1}$. Eqs. (60) and (61) are used to derived the moments
338 $\mu_n^{(i)}$ of Laplace transformed solutions given in Eqs. (32) and (35) for $i = 1, 2$ and $n = 0, 1, 2, 3$. Let us define

$$r = a_1 F \widetilde{\nu}_1 Pe, \quad \gamma = \sqrt{Pe(Pe + 4a_1 F\nu)}, \quad \delta_{1,2} = Pe \mp \gamma,$$

$$\chi_{1,2} = \frac{\gamma Pe^4}{64} + \frac{3\gamma^3 Pe^2}{32} + \frac{\gamma^5}{64} \mp r^2 Pe \mp \frac{3r Pe^3}{4} \mp \frac{Pe^5}{8},$$

$$\chi_{3,4} := \frac{\gamma^3 Pe}{8} \mp \frac{\gamma^2 (Pe^2 + 2r)}{8}, \quad \chi_5 := \frac{\gamma^3 (Pe^2 - 4r) - \gamma Pe^4}{32}, \quad \chi_6 := F(a_1 - a_2)Pe + (1 + a_2 F)r,$$

$$\chi_{7,8} := \frac{Pe^2\, e^{Pe}}{2}\left(\left[\frac{F(a_1 - a_2)Pe}{4} + \frac{r(1 + a_1 F)}{8}\right]\gamma^3 + \frac{rPe^2(1 + a_1 F)\gamma}{8} \mp \frac{F(a_1 - a_2)Pe^4}{4}\right.$$

$$\left. \mp \frac{3Fr(a_1 - a_2)Pe^2}{2} \mp \frac{r(1 + a_1 F)^3 Pe}{4} \mp r^2(1 + a_1 F)Pe \mp r^2[1 + (3a_1 - 2a_2)F]\right). \tag{A-1}$$

339 By using Eq. (60), the zeroth moments are given as

$$\mu_0^{(1)} = C_{1,\text{inj}}\tau_{\text{inj}} e^{\frac{\delta_1}{2}}, \quad \mu_0^{(2)} = C_{1,\text{inj}}\tau_{\text{inj}}(1 - e^{\frac{\delta_1}{2}}). \tag{A-2}$$

340 From Eq. (A-2), we get $\mu_0^{(1)} + \mu_0^{(2)} = C_{1,\text{inj}}\tau_{\text{inj}}$, as $C_{2,\text{inj}} = 0$ is considered.
341 The first moments are calculated by using the Eq. (61) for $n = 1$

$$\mu_1^{(1)} = \frac{\tau_{\text{inj}}}{2} + \frac{Pe(1 + a_1 F)}{\gamma}, \tag{A-3}$$

$$\mu_1^{(2)} = \frac{\tau_{\text{inj}}}{2} + \frac{Pe[\gamma F(a_2 - a_1) - r(1 + a_1 F)]e^{\frac{\delta_1}{2}} - \gamma[F(a_2 - a_1)Pe - r(1 + a_2 F)]}{r\gamma(1 - e^{\frac{\delta_1}{2}})}. \tag{A-4}$$

342 The second moments are expressed as

$$\mu_2^{(1)} = \frac{\tau_{\text{inj}}^2}{3} + \frac{Pe(1 + a_1 F)\tau_{\text{inj}}}{\gamma} + \frac{Pe^2(1 + a_1 F)(\gamma + 2)}{\gamma^3} + \frac{2Pea_1 F(1 - \epsilon)}{\gamma \widetilde{k}_1}, \tag{A-5}$$

$$\mu_2^{(2)} = \frac{\tau_{\text{inj}}^2}{3} + \left[\frac{Pe\left(\gamma F(a_2 - a_1) - r(1 + a_1 F)\right)e^{\frac{\delta_1}{2}} - \gamma\left(F(a_2 - a_1)Pe - r(1 + a_2 F)\right)}{r\gamma\left(1 - e^{\frac{\delta_1}{2}}\right)}\right]\tau_{\text{inj}}$$
$$+ \frac{1}{1 - e^{\frac{\delta_1}{2}}}\left(e^{\frac{\delta_1}{2}}\left[-\frac{2Pea_1 F(1 - \epsilon)}{\gamma \widetilde{k}_1} - \frac{2PeF(1 - \epsilon)(a_1 \widetilde{k}_2 - a_2 \widetilde{k}_1)}{r \widetilde{k}_1 \widetilde{k}_2} - \frac{2Pe^2(1 + a_1 F)^2}{\gamma^3}\right.\right.$$
$$\left.- \frac{Pe^2 F^2(a_2 - a_1)^2}{r^2}\right] + \frac{2PeF(1 - \epsilon)(a_1 \widetilde{k}_2 - a_2 \widetilde{k}_1)}{r \widetilde{k}_1 \widetilde{k}_2} + \frac{Pe^2 F^2(a_2 - a_1)^2}{r^2} + \frac{2(1 + a_2 F)^2}{Pe}$$
$$\left.+ \frac{2a_2 F(1 - \epsilon)}{\widetilde{k}_2}\right) - \frac{Pe^2[\gamma F(a_2 - a_1) - r(1 + a_1 F)]^2 e^{\frac{\delta_1}{2}} - \gamma^2[F(a_2 - a_1)Pe - r(1 + a_2 F)]^2}{r^2\gamma^2(1 - e^{\frac{\delta_1}{2}})}. \tag{A-6}$$

343 The above equations are helpful to calculate the second central moments by using the given relations

$$\mu'^{(i)}_2 = \mu_2^{(i)} - \left(\mu_1^{(i)}\right)^2, \quad i = 1, 2. \tag{A-7}$$

344 Thus, the second central moments are given as

$$\mu'^{(1)}_2 = \frac{\tau_{\text{inj}}^2}{12} + \frac{2Pe\left[\gamma^2 a_1 F(1 - \epsilon) + Pe\widetilde{k}_1(1 + a_1 F)^2\right]}{\gamma^3 \widetilde{k}_1}, \tag{A-8}$$

$$\mu'^{(2)}_2 = \frac{\tau_{\text{inj}}^2}{12} + \frac{1}{1 - e^{\frac{\delta_1}{2}}}\left(e^{\frac{\delta_1}{2}}\left[-\frac{2Pea_1 F(1 - \epsilon)}{\gamma \widetilde{k}_1} - \frac{2PeF(1 - \epsilon)(a_1 \widetilde{k}_2 - a_2 \widetilde{k}_1)}{r \widetilde{k}_1 \widetilde{k}_2} - \frac{2Pe^2(1 + a_1 F)^2}{\gamma^3}\right.\right.$$
$$\left.- \frac{Pe^2 F^2(a_2 - a_1)^2}{r^2}\right] + \frac{2PeF(1 - \epsilon)(a_1 \widetilde{k}_2 - a_2 \widetilde{k}_1)}{r \widetilde{k}_1 \widetilde{k}_2} + \frac{Pe^2 F^2(a_2 - a_1)^2}{r^2} + \frac{2(1 + a_2 F)^2}{Pe}$$
$$\left.+ \frac{2a_2 F(1 - \epsilon)}{\widetilde{k}_2}\right) - \left[\frac{Pe^2[\gamma F(a_2 - a_1) - r(1 + a_1 F)]^2 e^{\frac{\delta_1}{2}} - \gamma^2[F(a_2 - a_1)Pe - r(1 + a_2 F)]^2}{r^2\gamma^2(1 - e^{\frac{\delta_1}{2}})}\right]$$
$$- \left[\frac{Pe[\gamma F(a_2 - a_1) - r(1 + a_1 F)]e^{\frac{\delta_1}{2}} - \gamma[F(a_2 - a_1)Pe - r(1 + a_2 F)]}{r\gamma(1 - e^{\frac{\delta_1}{2}})}\right]^2. \tag{A-9}$$

345 The third moments are given as

$$\mu_3^{(1)} = \frac{\tau_{\text{inj}}^3}{4} + \frac{Pe(1 + a_1 F)\tau_{\text{inj}}^2}{\gamma} + \left[\frac{Pe^2(1 + a_1 F)^2(\gamma + 2)}{\gamma^3} + \frac{2Pea_1 F(1 - \epsilon)}{\gamma \widetilde{k}_1}\right]\frac{3\tau_{\text{inj}}}{2}$$
$$+ \frac{Pe^3(1 + a_1 F)^3(\gamma^2 + 6\gamma + 12)}{\gamma^5} + \frac{6Pe^2 a_1 F(1 + a_1 F)(\gamma + 2)(1 - \epsilon)}{\gamma^3 \widetilde{k}_1} +$$
$$+ \frac{6Pea_1 F(1 - \epsilon)^2}{\gamma \widetilde{k}_1^2}. \tag{A-10}$$

$$\mu_3^{(2)} = \frac{\tau_{\text{inj}}^3}{4} + \left(\frac{Pe[\gamma F(a_2 - a_1) - r(1 + a_1 F)]e^{\frac{\delta_1}{2}} - \gamma[F(a_2 - a_1)Pe - r(1 + a_2 F)]}{r\gamma(1 - e^{\frac{\delta_1}{2}})}\right)\tau_{\text{inj}}^2$$

$$
+ \frac{3\tau_{\mathrm{inj}}}{2(1 - e^{\frac{\delta_1}{2}})} \left(e^{\frac{\delta_1}{2}} \left[\frac{-2Pe^2(1 + a_1F)^2}{\gamma^3} - \frac{Pe^2F^2(a_2 - a_1)^2}{r^2} - \frac{2Pea_1F(1 - \epsilon)}{\gamma \widetilde{k}_1} + \right. \right.
$$

$$
\left. - \frac{2PeF(1 - \epsilon)(a_1\widetilde{k}_2 - a_2\widetilde{k}_1)}{r\widetilde{k}_1\widetilde{k}_2} \right] + \frac{Pe^2F^2(a_2 - a_1)^2}{r^2} + \frac{2PeF(1 - \epsilon)(a_1\widetilde{k}_2 - a_2\widetilde{k}_1)}{r\widetilde{k}_1\widetilde{k}_2}
$$

$$
\left. + \frac{2(1 + a_2F)^2}{Pe} + \frac{2a_2F(1 - \epsilon)}{\widetilde{k}_2} \right)
$$

$$
- \left(\frac{Pe^2[\gamma F(a_2 - a_1) - r(1 + a_1F)]^2 e^{\frac{\delta_1}{2}} - \gamma^2[F(a_2 - a_1)Pe - r(1 + a_2F)]^2}{2r^2\gamma^2(1 - e^{\frac{\delta_1}{2}})} \right) 3\tau_{\mathrm{inj}}
$$

$$
- \frac{6Pe^3F^3(a_2 - a_1)^3}{r^3} - \frac{1}{(1 - e^{\frac{\delta_1}{2}})} \left[\frac{Pe^3 e^{\frac{\delta_1}{2}}(1 + a_1F)^3(\gamma^2 + 6\gamma + 12)}{\gamma^5} \right.
$$

$$
- \frac{3FPe^3 e^{\frac{\delta_1}{2}}(1 + a_1F)^2(a_2 - a_1)(\gamma + 2)}{r\gamma^3} + \frac{6F^2Pe^3(1 + a_1F)(a_2 - a_1)^2}{r^2\gamma}
$$

$$
\left. + \frac{6F(1 + a_2F)^2(a_2 - a_1)}{r} - \frac{(Pe^2 + 12)(1 + a_2F)^3}{Pe^2} \right]
$$

$$
+ \frac{12Pe^2F^2(a_2 - a_1)(1 - \epsilon)(a_2\widetilde{k}_1 - a_1\widetilde{k}_2)}{r^2\widetilde{k}_1\widetilde{k}_2} - \frac{e^{\frac{\delta_1}{2}}Pe^2(1 - \epsilon)}{(1 - e^{\frac{\delta_1}{2}})} \left[\frac{12a_1F(1 + a_1F)^2}{\gamma^3\widetilde{k}_1} \right.
$$

$$
\left. - \frac{6a_1F^2(a_2 - a_1)}{r\gamma\widetilde{k}_1} + \frac{6a_1F(1 + a_1F)}{\gamma^2\widetilde{k}_1} - \frac{6F(1 + a_1F)(a_2\widetilde{k}_1 - a_1\widetilde{k}_2)}{r\gamma\widetilde{k}_1\widetilde{k}_2} \right]
$$

$$
- \frac{1}{(1 - e^{\frac{\delta_1}{2}})} \left[\frac{-12a_2F(1 + a_2F)(1 - \epsilon)}{Pe\widetilde{k}_2} - \frac{6Pe^2F^2(1 + a_2F)(a_2 - a_1)^2}{r^2} \right]
$$

$$
- \frac{6PeF(1 - \epsilon)^2(a_2\widetilde{k}_1^2 - a_1\widetilde{k}_2^2)}{r\widetilde{k}_1^2\widetilde{k}_2^2} - \frac{1}{(1 - e^{\frac{\delta_1}{2}})} \left[\frac{6Pea_1Fe^{\frac{\delta_1}{2}}(1 - \epsilon)^2}{\gamma\widetilde{k}_1^2} + \frac{6Pea_2F^2(1 - \epsilon)(a_2 - a_1)}{r\widetilde{k}_2} \right.
$$

$$
\left. + \frac{3PeF(1 + a_2F)^2(a_2 - a_1)}{r} + \frac{6PeF(1 - \epsilon)(1 + a_2F)(a_2\widetilde{k}_1 - a_1\widetilde{k}_2)}{r\widetilde{k}_1\widetilde{k}_2} \right]
$$

$$
- \frac{1}{(1 - e^{\frac{\delta_1}{2}})} \left[\frac{-6(1 + a_2F)^3}{Pe} - \frac{6a_2F(1 - \epsilon)^2}{\widetilde{k}_2^2} - \frac{6a_2F(1 - \epsilon)(1 + a_2F)}{\widetilde{k}_2} \right]. \tag{A-11}
$$

Finally, the third central moments can be deduced from the given relations

$$
\mu_3'^{(i)} = \mu_3^{(i)} - 3\mu_1^{(i)}\mu_2^{(i)} + 2\left(\mu_1^{(i)} \right)^3, \quad i = 1, 2. \tag{A-12}
$$

The expressions of third central moments were very lengthy. Therefore, only plots of these moments are shown in the test problems.

A.2 Irreversible reaction with Danckwerts BCs

Here, the moments are derived of the solutions given in Eqs. (40) and (41).
The zeroth moments are given as

$$
\mu_0^{(1)} = \frac{-4C_{1,\mathrm{inj}}\tau_{\mathrm{inj}}\gamma Pe\, e^{Pe}}{\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}}}, \quad \mu_0^{(2)} = C_{1,\mathrm{inj}}\tau_{\mathrm{inj}} \left[1 + \frac{4\gamma Pe\, e^{Pe}}{\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}}} \right]. \tag{A-13}
$$

From Eq. (A-13), it follows that $\mu_0^{(1)} + \mu_0^{(2)} = C_{1,\mathrm{inj}}\tau_{\mathrm{inj}}$, as $C_{2,\mathrm{inj}} = 0$ is considered.
The first moments take the form

$$
\mu_1^{(1)} = \frac{\tau_{\mathrm{inj}}}{2} - \frac{2Pe(1 + a_1F)}{\gamma^2(\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}})} \left[\gamma(2r + Pe^2)\left(e^{\frac{\delta_1}{2}} + e^{\frac{\delta_2}{2}} \right) - (4r(1 + Pe) + Pe^3)\left(e^{\frac{\delta_1}{2}} - e^{\frac{\delta_2}{2}} \right) \right]. \tag{A-14}
$$

$$
\mu_1^{(2)} = \frac{32\tau_{\mathrm{inj}}\left(\chi_1 e^{\delta_1} + [\chi_5 e^{\frac{\delta_2}{2}} - Pe\, e^{Pe}\chi_3]e^{\frac{\delta_1}{2}} + [\chi_2 e^{\frac{\delta_2}{2}} - Pe\, e^{Pe}\chi_4]e^{\frac{\delta_2}{2}} \right)}{\gamma(\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}})(\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}} + 4\gamma Pe\, e^{Pe})}
$$

$$+ \frac{64\left[\chi_1\chi_6 e^{\delta_1} + [\chi_5\chi_6 e^{\frac{\delta_2}{2}} - \chi_7]e^{\frac{\delta_1}{2}} + [\chi_2\chi_6 e^{\frac{\delta_2}{2}} - \chi_8]e^{\frac{\delta_2}{2}}\right]}{r\gamma(\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}})(\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}} + 4\gamma Pe\, e^{Pe})}.$$

(A-15)

354 The second and third central moments are not given here due to their lengthy expressions.

355 ## A.3 Reversible reaction with Dirichlet BCs

356 The Eqs. (60) and (61) are used to derived the moments $\mu_n^{(i)}$ of Laplace transformed solutions given in Eqs. (53)
357 and (54) for $i = 1, 2$ and $n = 0, 1, 2, 3$. Let us define

$$R_1 = (a_1\widetilde{\nu}_1 + a_2\widetilde{\nu}_2)FPe, \quad \gamma_{1,2} = \sqrt{Pe^2 + 2R_1 \mp 2\sqrt{P + R_1^2}}, \quad \delta_{1,2} = Pe \mp \gamma_1$$

$$\delta_{3,4} = Pe \mp \sqrt{Pe^2 + 2R_1 + 2\sqrt{P + R_1^2}}, \quad \chi_{1,2} := W \mp \sqrt{P + R_1^2},$$

$$\chi_3 = 2(P - W^2 + R_1^2)\{(a_1F + a_2)\epsilon - a_2\}\gamma_1 + \{(2 + a_1F - a_2)\epsilon + a_2\}(P + R_1^2)^{\frac{3}{2}}$$
$$+ W\left[W\{(a_1F + a_2)\epsilon - a_2\}\sqrt{P + R_1^2} - 2\epsilon(P + R_1^2)(1 + a_1F)\right],$$

$$\chi_4 = -2(P - W^2 + R_1^2)\{(a_1F + a_2)\epsilon - a_2\}\gamma_2 + \{(2 + a_1F - a_2)\epsilon + a_2\}(P + R_1^2)^{\frac{3}{2}}$$
$$+ W\left[W\{(a_1F + a_2)\epsilon - a_2\}\sqrt{P + R_1^2} + 2\epsilon(P + R_1^2)(1 + a_1F)\right],$$

$$\chi_5 = -2W\{(a_1F + a_2)\epsilon - a_2\}\gamma_1 + W\{(a_2 + a_1F)\epsilon - a_2\}\sqrt{P + R_1^2}$$
$$- (P + R_1^2)\{(2 - a_2 + a_1F)\epsilon + a_2\},$$

$$\chi_6 = 2W\{(a_1F + a_2)\epsilon - a_2\}\gamma_2 + W\{(a_2 + a_1F)\epsilon - a_2\}\sqrt{P + R_1^2}$$
$$+ (P + R_1^2)\{(2 - a_2 + a_1F)\epsilon + a_2\}.$$

(A-16)

358 Using Eq. (60), the zeroth moments can be calculated as

$$\mu_0^{(1)} = \frac{C_{1,\text{inj}}\tau_{\text{inj}}(\chi_2 e^{\frac{\delta_3}{2}} - \chi_1 e^{\frac{\delta_1}{2}})}{2\sqrt{P + R_1^2}}, \qquad \mu_0^{(2)} = \frac{r_3 C_{1,\text{inj}}\tau_{\text{inj}}}{\sqrt{P + R_1^2}}\left(e^{\frac{\delta_1}{2}} - e^{\frac{\delta_3}{2}}\right).$$

(A-17)

359 The first moments are derived by using Eq. (61) for $n = 1$

$$\mu_1^{(1)} = \frac{\tau_{\text{inj}}}{2} + \frac{Pe(\gamma_2\chi_3 e^{\frac{\delta_1}{2}} + \gamma_1\chi_4 e^{\frac{\delta_3}{2}})}{2\epsilon\gamma_1\gamma_2(P + R_1^2)(\chi_2 e^{\frac{\delta_3}{2}} - \chi_1 e^{\frac{\delta_1}{2}})},$$

(A-18)

$$\mu_1^{(2)} = \frac{\tau_{\text{inj}}}{2} + \frac{Pe(\gamma_2\chi_5 e^{\frac{\delta_1}{2}} + \gamma_1\chi_6 e^{\frac{\delta_3}{2}})}{2\epsilon\gamma_1\gamma_2(P + R_1^2)(e^{\frac{\delta_3}{2}} - e^{\frac{\delta_1}{2}})}.$$

(A-19)

360 Moreover, the expressions of analytical $\mu'^{(i)}_2$ and $\mu'^{(i)}_3$ were very lengthy. Therefore, plots of second and third central
361 moments are shown in Figure 6.

362 ## A.4 Reversible reaction with Danckwerts BCs

363 Here, the moments are derived of the solutions given in Eqs. (58) and (59). The zeroth moments are

$$\mu_0^{(1)} = \frac{2C_{1,\text{inj}}\tau_{\text{inj}}Pe\, e^{Pe}}{\sqrt{P + R_1^2}}\left[\frac{\chi_1\gamma_1}{\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}}} - \frac{\chi_2\gamma_2}{\delta_3^2 e^{\frac{\delta_3}{2}} - \delta_4^2 e^{\frac{\delta_4}{2}}}\right],$$

(A-20)

$$\mu_0^{(2)} = \frac{-4r_3 C_{1,\text{inj}}\tau_{\text{inj}}Pe\, e^{Pe}}{\sqrt{P + R_1^2}}\left[\frac{\gamma_1}{\delta_1^2 e^{\frac{\delta_1}{2}} - \delta_2^2 e^{\frac{\delta_2}{2}}} - \frac{\gamma_2}{\delta_3^2 e^{\frac{\delta_3}{2}} - \delta_4^2 e^{\frac{\delta_4}{2}}}\right].$$

(A-21)

Other moments are not presented here due to their lengthy expressions.

Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflict of interest.

Ethical approval: This article does not contain any studies with human participants or animals performed by any of the authors.

References

1. Ganetsos, G., Barker, P.E.: Preparative and production scale chromatography. Vol. 61, Marcel Dekker, Inc., New York, 375-523, (1993).
2. Guiochon, G., Lin, B.: Modeling for preparative chromatography. Academic Press, (2003).
3. Guiochon, G., Shirazi, G., Katti, M.: in: Fundamentals of preparative and nonlinear chromatography, 2nd ed., Elsevier Inc., Netherlands, (2006).
4. Mazzotti, M., Kruglov, A., Neri, B., Gelosa, D., Morbidelli, M.: A continuous chromatographic reactor: SMBR. Chem. Eng. Sci. 51, 1827-1836, (1996).
5. Yamaoka, K., Nakagawa, T.: Moment analysis for reaction chromatography. J. Chromatogr. A 117, 1-10, (1976).
6. Takeuchi, K., Uraguchi, Y.: Separation conditions of the reactant and the product with a chromatographic moving bed reactor. J. Chem. Eng. Japan 9, 164-166, (1976).
7. Takeuchi, K., Uraguchi, Y.: Basic design of chromatographic moving-bed reactors for product refining. J. Chem. Engng Japan 9, 246-248, (1976).
8. Takeuchi, K., Uraguchi, Y.: The effect of the exhausting section on the performance of a chromatographic moving-bed reactor. J. Chem. Engng Japan 10, 72-74, (1977).
9. Takeuchi, K., Uraguchi, Y.: Experimental studies of a chromatographic moving-bed reactor-catalytic oxidation of carbon monoxide on activated alumina as a model reactor. J. Chem. Eng. Japan 10, 455-460, (1977).
10. Takeuchi, K., Miyauchi, T., Uraguchi, Y.: Computational studies of a chromatographic moving bed reactor for consecutive and reversible reactions. J. Chem. Eng. Japan 11, 216-220, (1978).
11. Schweich, D., Villermaux, J.: The chromatographic reactor. A new theoretical approach. Ind. Eng. Chem. Fundamen. 17, 1-7, (1978).
12. Villermaux, J.: The chromatographic reactor, in percolation processes: Theory and applications. A.E. Rodrigues and D. Tondeur (Eds.), Sijthoff & Noordhoff, Maryland, (1981).
13. Cho, B.K., Aris, R., Carr, R.W.: The mathematical theory of a countercurrent catalytic reactor. Proc. R. Sot. Lond. 383, 147-189, (1982).
14. Petroulas, T., Aris, R., Carr, R.W.: Analysis of the counter-current moving-bed chromatographic reactor, Comp. Math. Appl. 11, 5-34, (1985).
15. Carta, G.: Simultaneous reaction and chromatography, in: Chromatographic and membrane processes in biotechnology (Edited by C. A. Costa and J. S. Cabral), 429-447, NATO ASI, Kluwer Academic Publishers, Deventer, (1991).
16. Binous, H., McCoy, B.: Chromatographic reactions of the three components: Application to separations. Chem. Eng. Sci. 47, 4333-4343, (1992).
17. Sardin, M., Schweich, D., Villermaux, J., Ganetsos, G., Barker, P.E. (Eds.): Preparative fixed-bed chromatographic reactor, Preparative and production scale chromatography, Marcel Dekker Inc., New York, USA, (1993).
18. Lin, B., Song, F., Guiochon, G.: Analytical solution of the ideal, nonlinear model of reaction chromatography for a reaction A← B and a parabolic isotherm. J. Chromatogr. A 1003, 91-100, (2003).
19. Borren, T., Fricke, J., Schmidt-Traub, H. (Eds.): Chromatographic reactors in preparative chromatography of fine chemicals and pharmaceutical agents. Wiley-VCH Verlag, Weinheim, 371-395, (2005).
20. Fricke, J., Schmidt-Traub, H., Kawase, M.: Chromatographic reactor. Ullmann's Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag, Weinheim, (2005).
21. Javeed, S., Qamar, S., Seidel-Morgenstern, A., Warnecke, G.: A discontinuous Galerkin method to solve chromatographic models, J. Chromatogr. A 1218, 7137-7146, (2011).
22. Javeed, S., Qamar, S., Seidel-Morgenstern, A., Warnecke, G.: Parametric study of thermal effects in reactive liquid chromatography. Chem. Eng. J. 191, 426-440, (2012).
23. Qamar, S., Bibi, S., Khan, F.U., Shah, M., Javeed, S., Seidel-Morgenstern, A.: Irreversible and reversible reactions in a liquid chromatographic column: analytical solutions and moment analysis, Ind. Eng. Chem. res. 53, 2461-2472, (2014).
24. Ruthven, D.M.: Principles of adsorption and adsorption processes. Wiley-Interscience, New York, (1984).
25. Van Genuchten, M.Th.: Analytical solutions for chemical transport with simultaneous adsorption, zeroth-order production and first order decay. J. Hydrology 49, 213-233, (1981).
26. Rice, R.G., Do, D.D.: Applied mathematics and modeling for chemical engineers, Wiley-Interscience, New York, (1995).
27. Durbin, F.: Numerical Inversion of Laplace Transforms: An efficient improvement to Dubner and Abate's Method. The Computer Journal 17, 371-376, (1974).

28. Schneider, P., Smith, J.M.: Adsorption rate constants from chromatography, AIChE J. 14, 762-771, (1968).
29. Mehta, R.V., Merson, R.L. , McCoy, B.J.: Hermite polynomial representation of chromatography elution curves. J. Chromatography A 88, 1-6, (1974).
30. Linek, F., Duduković, M.P.: Representation of breakthrough curves for fixed-bed adsorbers and reactors using moments of the impulse response. Chem. Eng. J. 23, 31-36, (1982).
31. Javeed, S., Qamar, S., Ashraf, W., Warnecke, G., Seidel-Morgenstern, A.: Analysis and numerical investigation of two dynamic models for liquid chromatography, Chem. Eng. Sci. 90, 17-31, (2013).
32. Qamar, S., Abbasi, J.N., Javeed, S., Shah, M., Khan, F.U., Seidel-Morgenstern, A.: Analytical solutions and moment analysis of chromatographic models for rectangular pulse injections. J. Chromatogr. A 1315, 92-106, (2013).
33. Suzuki, M., Smith, J.M.: Kinetic studies by chromatography. Chem. Eng. Sci. 26 221-235, (1971).
34. Bibi, S., Qamar, S., Seidel-Morgenstern, A.: Irreversible and reversible reactive chromatography: analytical solutions and moment analysis for rectangular pulse injections. J. Chromatogr. A 1385, 49-62, (2015).
35. Quezada, C.R., Clement, T.P., Lee, K.K.: Generalized solution to multi-dimensional multi-species transport equations coupled with a first-order reaction network involving distinct retardation factors. Advances in water resources 27, 507-520, (2004).
36. Abramowitz, M., Stegun, I.A.: Handbook of mathematical functions. Dover, New York, N.Y, (1970).
37. Carslaw, H.S., Jaeger, J.D.: Conduction of heat in solids. Oxford Unversity Press, London, 2nd ed, (1959).
38. Javeed, S., Qamar, S., Seidel-Morgenstern, A., Warnecke, G.: Efficient and accurate numerical simulation of nonlinear chromatographic processes. J. Comput. Chem. Eng. 35, 2294-2305, (2011).
39. Danckwerts, P.V.: Continuous flow systems. Chem. Eng. Sci. 2, 1-9, (1953).
40. Koren, B.: A robust upwind discretization method for advection, diffusion and source terms. In C. B. Vreugdenhil, B. Koren, editors, Numerical Methods for Advection-Diffusion Problems, Volume 45 of Notes on Numerical Fluid Mechanics, chapter 5, pages 117-138, Vieweg Verlag, Braunschweig, (1993).
41. Trapp, O., Schurig, V.: ChromWin A computer program for the determination of enantiomerization barriers in dynamic chromatography. Comput. Chem. 25, 187-195, (2001).
42. Trapp, O., Trapp, G., Schurig, V.: Direct calculation and computer simulation of the enantiomerization barrier of oxazepam in dynamic HPLC experiments-a comparative study. J. Biochem. Biophys. Methods 54, 301-313, (2002).

Table 1 Parameters for two-component RLKM.

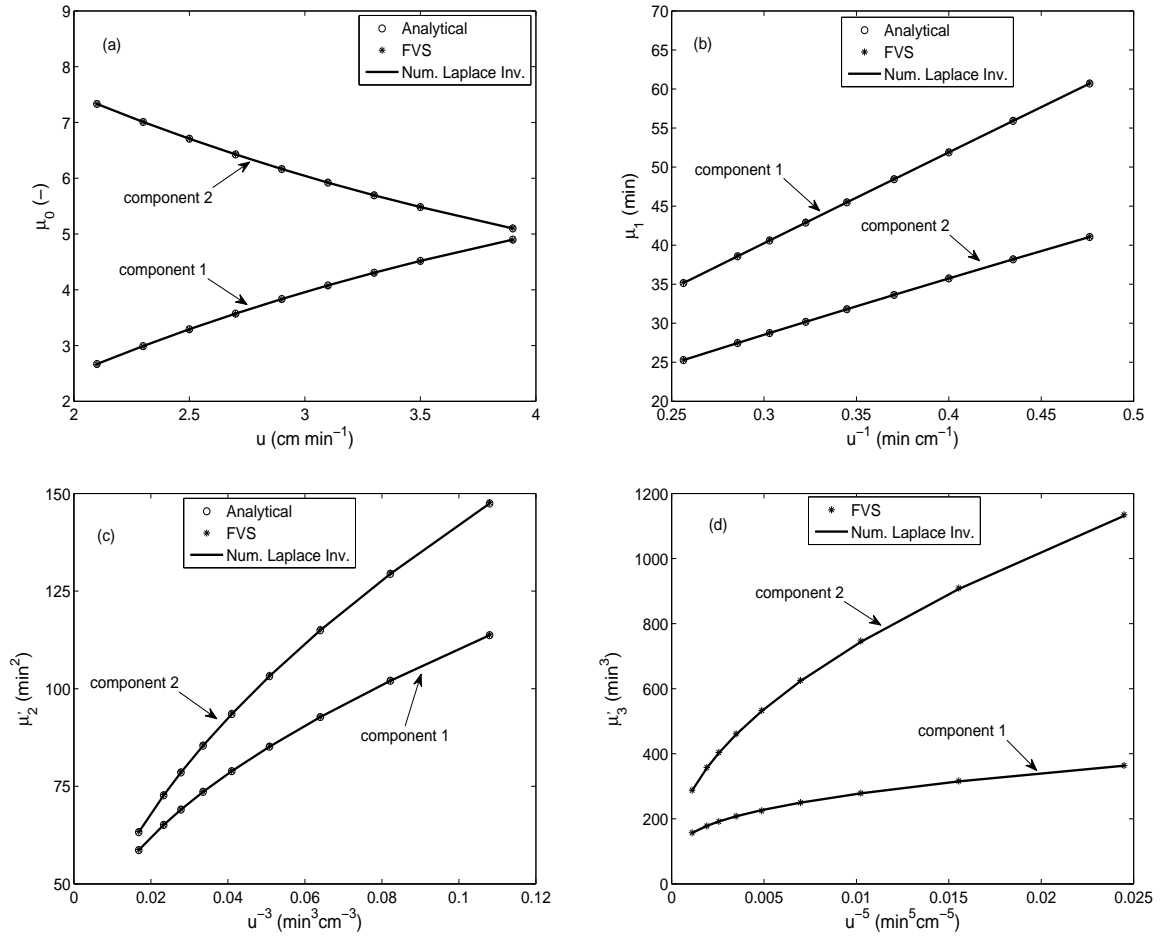| Parameters	values
Length of column	$L_{\max} = 25.0\ cm$
Diameter of column	$d = 0.46\ cm$
Porosity	$\epsilon = 0.35$
Mobile phase velocity	$u = 3.0\ cm(min^{-1})$
Time of injection	$t_{\mathrm{inj}} = 10\ min$
Peclet number	$Pe = 500$
Initial concentration of i-th component	$c_{i,\mathrm{init}} = 0\ gL^{-1}$
Adsorption equilibrium constant for component 1	$a_1 = 2.0$
Adsorption equilibrium constant for component 2	$a_2 = 0.5$
Mass transfer coefficient for component 1	$k_1 = 1\ min^{-1}$
Mass transfer coefficient for component 2	$k_2 = 1\ min^{-1}$
Liquid phase reaction rate constant (component 1)	$\eta_1 = 0.05\ min^{-1}$
Liquid phase reaction rate constant (component 2)	$\eta_2 = 0.1\ min^{-1}$
Solid phase reaction rate constant (component 1)	$\nu_1 = 0.03\ min^{-1}$
Solid phase reaction rate constant (component 2)	$\nu_2 = 0.06\ min^{-1}$
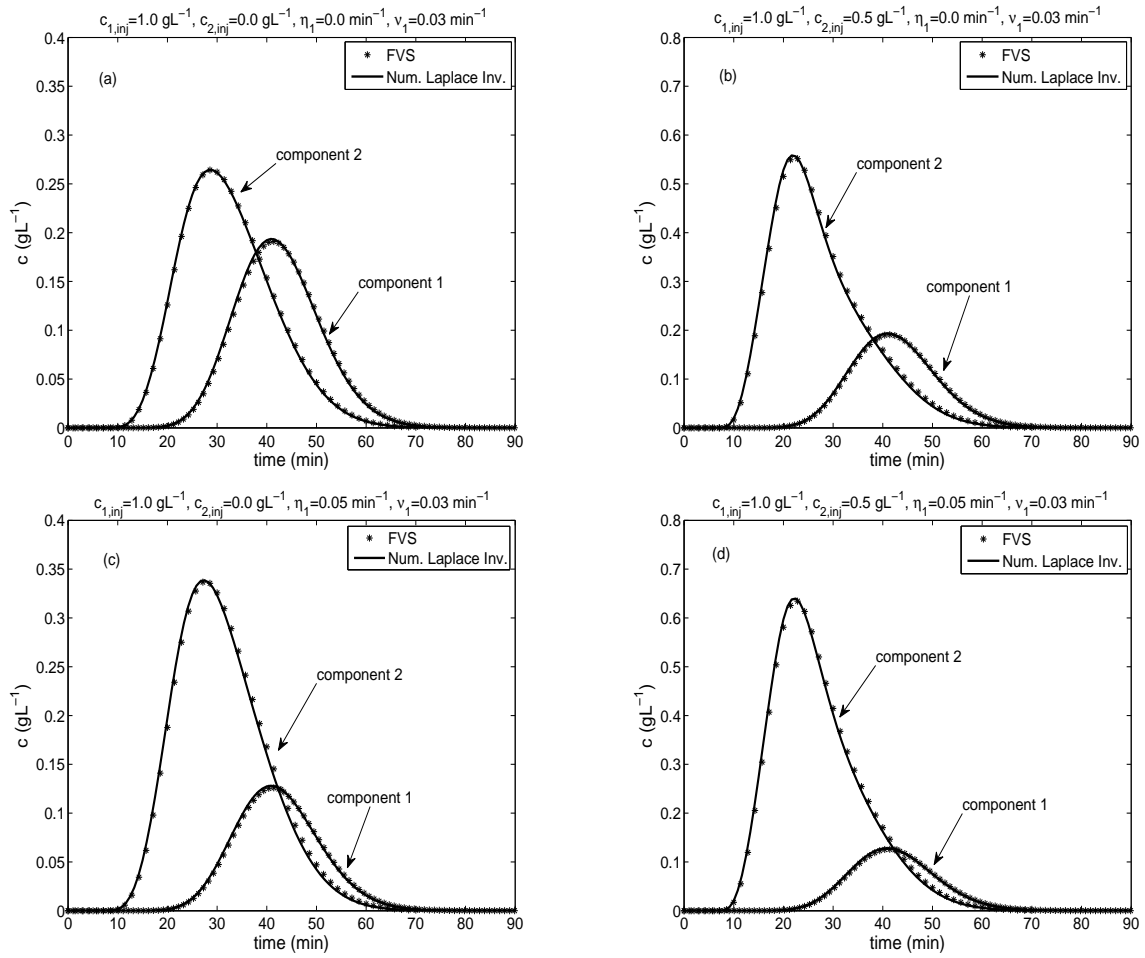
Fig. 1 Irreversible reaction: Plots (a)&(b): Solutions for Dirichlet BCs at $x = 1$ with zero liquid phase reaction. Plots (c)&(d): Comparison of solutions at $x = 1$ for both solid and liquid phases reactions using Dirichlet BCs. Here, $c_{i,\text{init}} = 0\,gL^{-1}$ $(i = 1, 2)$ and other parameters are given in Table 1.
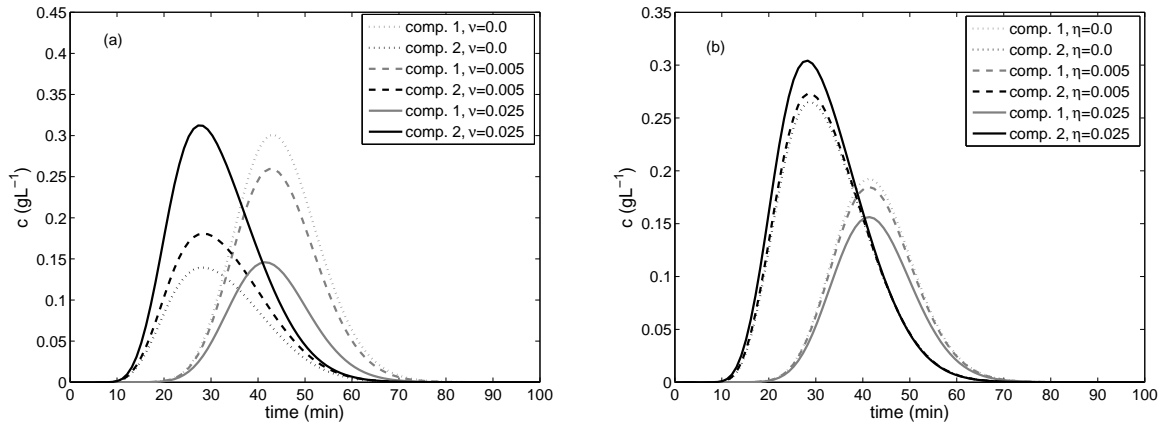

Fig. 2 Irreversible reaction: Plot (a): Concentration profiles at $x = 1$ for different values of the solid phase reaction rate constant. Plot (b): Concentration profiles at $x = 1$ for different values of liquid phase reaction rate constant. Other parameters are given in Table 1.
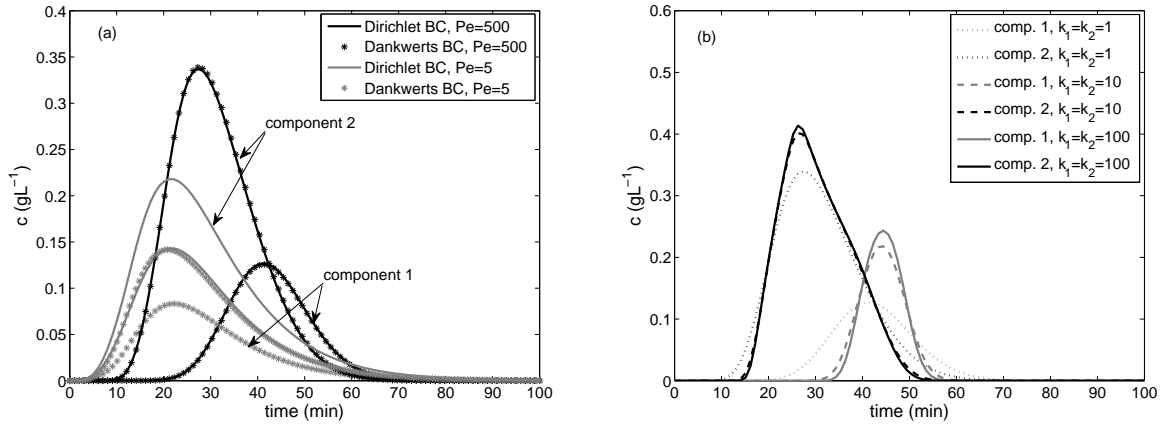
Fig. 3 Irreversible reaction: Plot (a): Effect of BCs for different Peclet numbers with $c_{1,inj} = 1\,gL^{-1}$, $c_{2,inj} = 0\,gL^{-1}$ and $c_{i,init} = 0\,gL^{-1}$ for $i = 1,2$. Plot (b): Effect of mass transfer coefficient on the concentration profiles. Other parameters are given in Table 1.

Fig. 4 Moments of irreversible reaction with Dirichlet BCs considering different values of u for $\eta = 0.0\,min^{-1}$ and $\nu = 0.03\,min^{-1}$. Here, $c_{i,init} = 0\,gL^{-1}$ $(i = 1,2)$, $c_{1,inj} = 1\,gL^{-1}$, and $c_{2,inj} = 0\,gL^{-1}$. Other parameters are listed in Table 1.
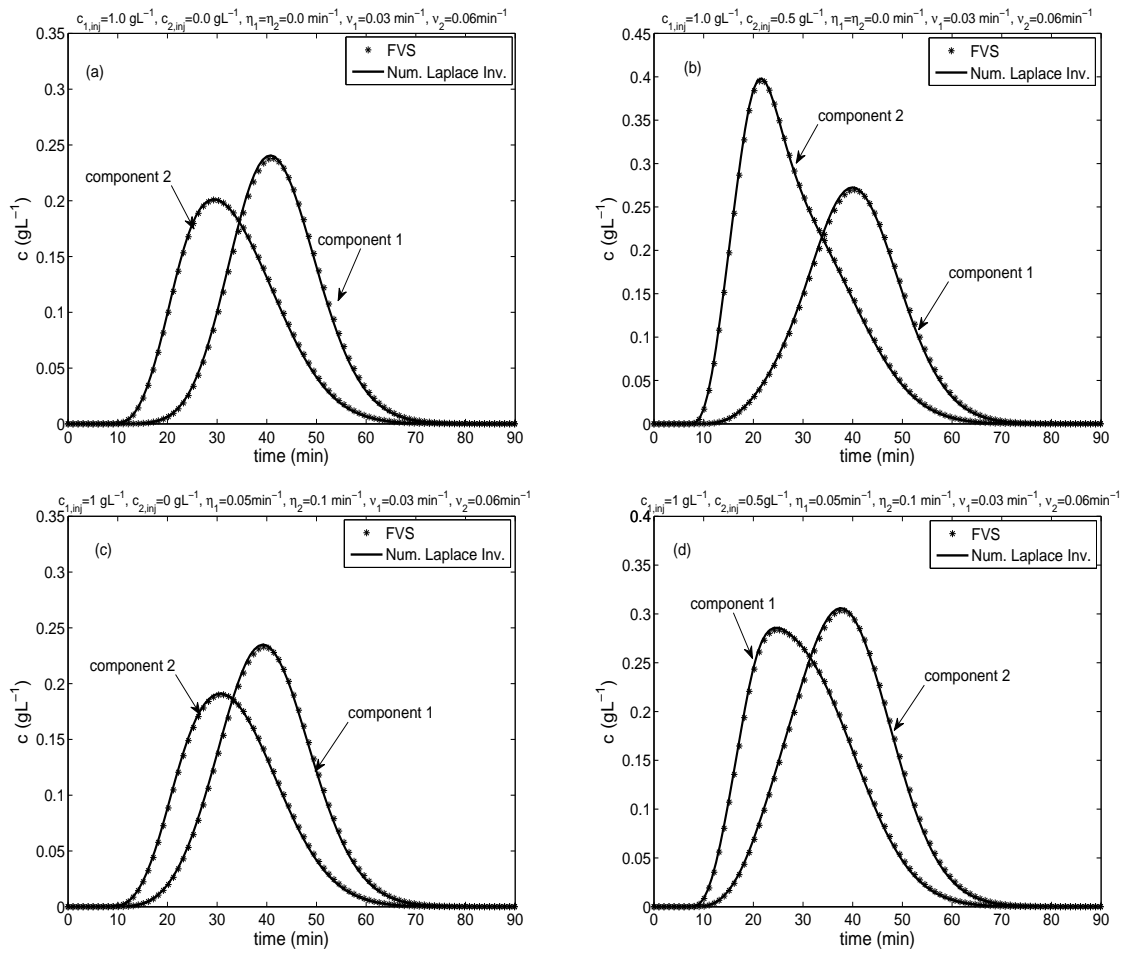
Fig. 5 Reversible reaction, Plots (a)&(b): Solutions for Dirichlet BCs at $x = 1$ with only solid phase reaction. Plots (c)&(d): Comparison of solutions at $x = 1$ for Dirichlet BCs and both liquid and solid phase reactions. Here, $c_{i,\text{init}} = 0\, gL^{-1}$ $(i = 1, 2)$ and other parameters are given in Table 1.
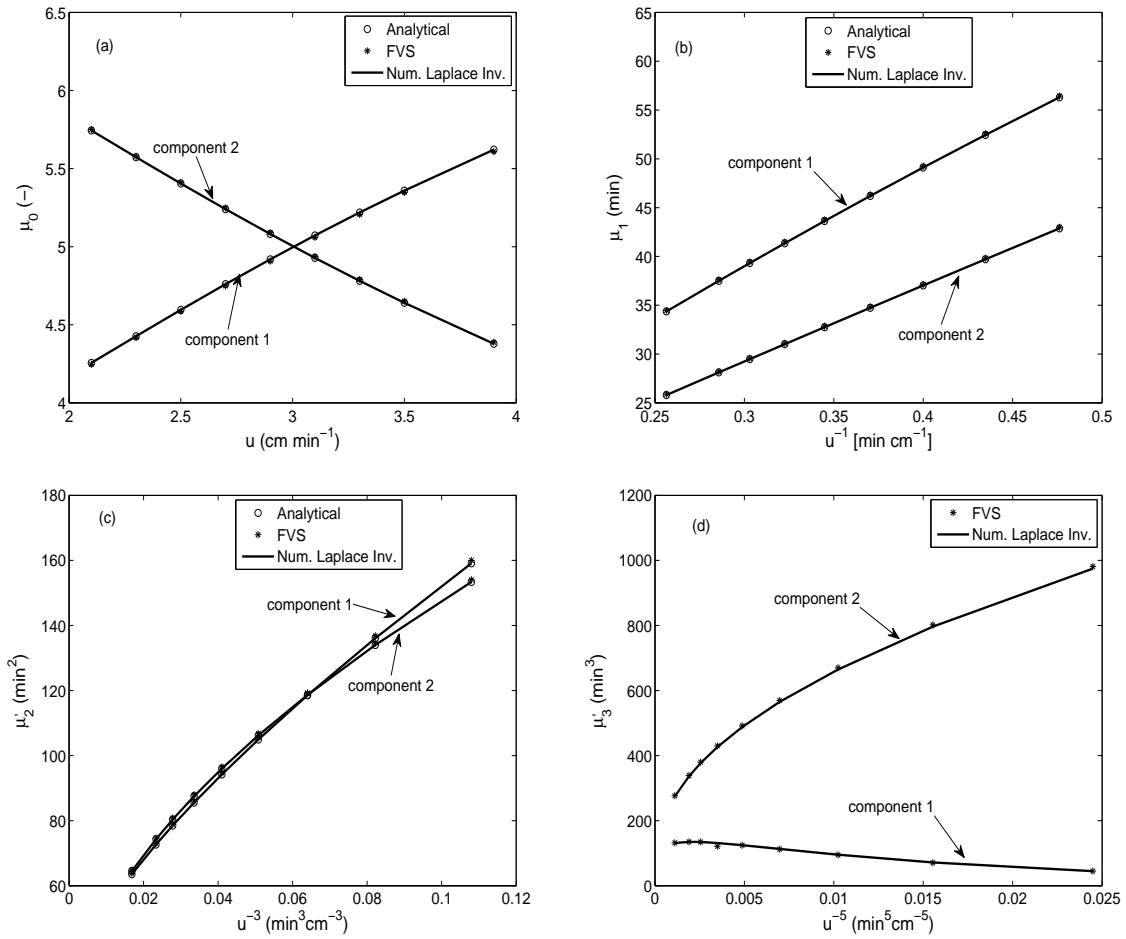
Fig. 6 Moments of reversible reaction with Dirichlet BCs considering different values of u for $\eta_1 = \eta_2 = 0\,min^{-1}$, $\nu_1 = 0.03\,min^{-1}$, $\nu_2 = 0.06\,min^{-1}$. Here, $c_{i,\mathrm{init}} = 0\,gL^{-1}$ for $i = 1, 2$, $c_{1,\mathrm{inj}} = 1\,gL^{-1}$, and $c_{2,\mathrm{inj}} = 0\,gL^{-1}$. Other parameters are listed in Table 1.